

NUTRIENT MASS BALANCE AND TRENDS, MOBILE RIVER BASIN, ALABAMA, GEORGIA, AND MISSISSIPPI¹

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ABSTRACT: A nutrient mass balance – accounting for nutrient inputs from atmospheric deposition, fertilizer, crop nitrogen fixation, and point source effluents; and nutrient outputs, including crop harvest and storage – was calculated for 18 subbasins in the Mobile River Basin, and trends (1970 to 1997) were evaluated as part of the U.S. Geological Survey National Water Quality Assessment (NAWQA) Program. Agricultural nonpoint nitrogen and phosphorus sources and urban nonpoint nitrogen sources are the most important factors associated with nutrients in this system. More than 30 percent of nitrogen yield in two basins and phosphorus yield in eight basins can be attributed to urban point source nutrient inputs. The total nitrogen yield (1.3 tons per square mile per year) for the Tombigbee River, which drains a greater percentage of agricultural (row crop) land use, was larger than the total nitrogen yield (0.99 tons per square mile per year) for the Alabama River. Decreasing trends of total nitrogen concentrations in the Tombigbee and Alabama Rivers indicate that a reduction occurred from 1975 to 1997 in the nitrogen contributions to Mobile Bay from the Mobile River. Nitrogen concentrations also decreased (1980 to 1995) in the Black Warrior River, one of the major tributaries to the Tombigbee River. Total phosphorus concentrations increased from 1970 to 1996 at three urban influenced sites on the Etowah River in Georgia. Multiple regression analysis indicates a distinct association between water quality in the streams of the Mobile River drainage basin and agricultural activities in the basin.

(KEY TERMS: water quality; nonpoint source pollution; mass balance; nutrient loads; nutrient trends; correlation analysis; Mobile River.)

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INTRODUCTION

Nutrients, such as nitrogen and phosphorus, are essential for a healthy and diverse aquatic environment. Excessive amounts of nutrients, however, can have undesirable effects on water quality, resulting in proliferation of plant life and changes in the biological community. High concentrations of nutrients also can result in potential human health risks associated with the growth of harmful algal blooms, most recently evidenced by *Pfiesteria* outbreaks along the Gulf and East Coasts. Recurring nutrient overenrichment of a waterbody often is associated with low dissolved oxygen, fish kills, algal blooms, overabundance of macrophytes, increased sediment accumulation rates, and species changes for flora and fauna (USEPA, 2000).

In the 1998 lists of impaired waters, the States reported that nutrients were the second leading cause of impairments to water quality (USEPA, 2000). Information regarding the sources and transport of nutrients is important for providing background information on nutrient effects on designated uses and for developing potential control strategies. This article presents the first systematic estimation of nutrient input and output fluxes for major river basins in the Mobile River Basin. Results of the study, which was conducted as part of the U.S. Geological Survey's (USGS) National Water Quality Assessment (NAWQA) Program (Hirsch *et al.*, 1988), provide estimates of total nutrient inputs for 18 subbasins (Figure 1; Table 1). These subbasins were USGS gaged

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sampling sites with continuous streamflow record and sufficient water quality data to allow instream nutrient load estimates. The instream load is considered the final output of the nutrient mass balance for the system, Equation (1).

In the mass balance, nutrient sources, or inputs, include point sources (such as municipal wastewater-treatment effluent), atmospheric precipitation, fertilizer, and animal waste. Nutrient removal from the

basin by crop harvest is also estimated. The difference between the estimated inputs and outputs represents the nutrients that are stored and processed by the basin and do not reach the stream.

$$\begin{array}{c} A + F + C + W + P = L + H + S \\ \text{Inputs} \qquad \qquad \qquad \text{Outputs} \end{array} \quad (1)$$

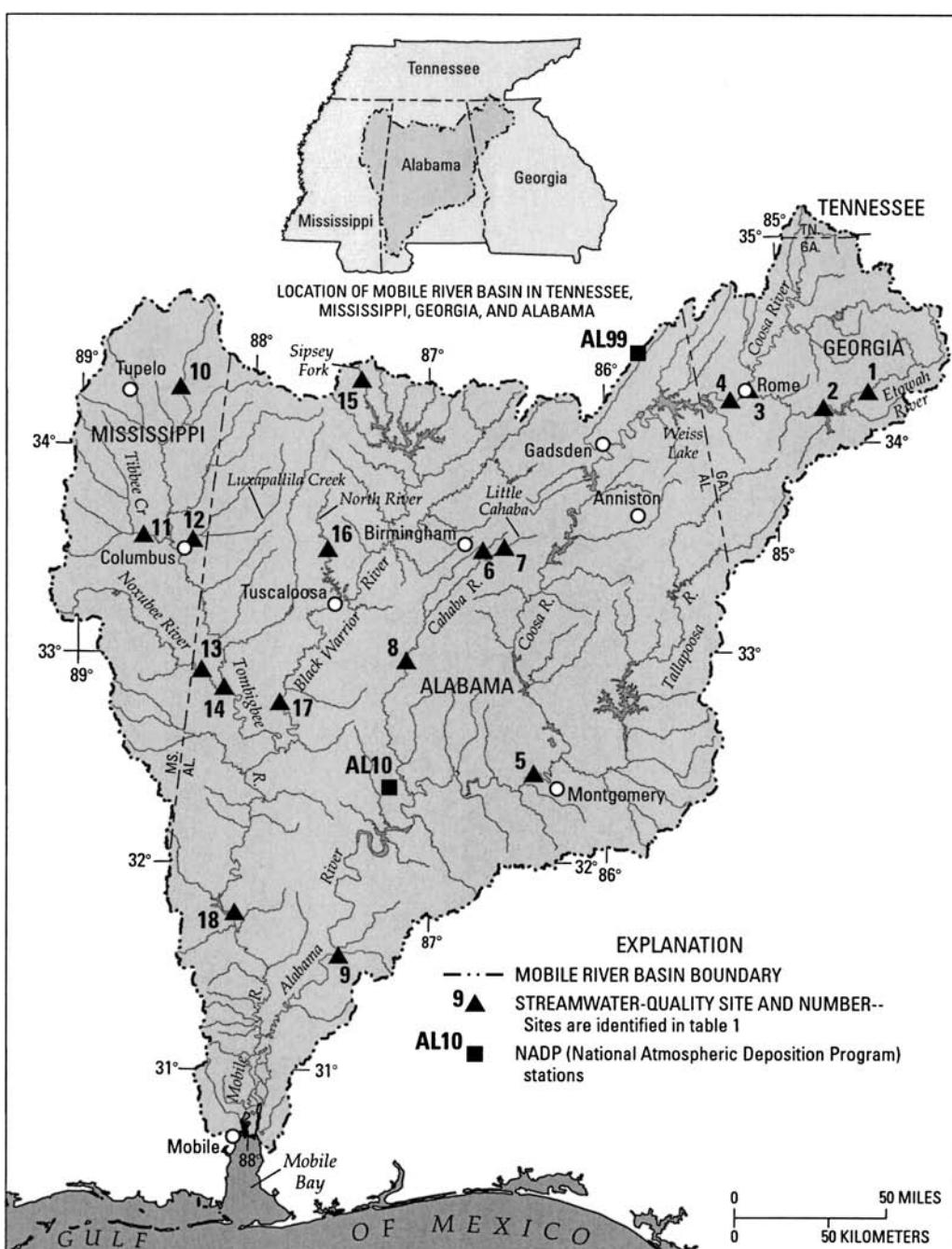


Figure 1. Location of the Mobile River Basin and Streamwater Quality Sites Used for Nutrient Assessment and NADP Stations.

TABLE 1. U.S. Geological Survey Station Name, Number, Drainage Area, and Land Use for Study Subbasin Sites in the Mobile River Basin (mi^2 , square mile).

Map No. (Figure 1)	Station Name	USGS Station Number*	Drainage Area (mi^2)	Agriculture	Land Use (percent) Urban	Forest
1	Etowah River at Canton, Georgia	02392000	613	8.6	0.41	89
2	Etowah River at Allatoona Dam above Cartersville, Georgia	02394000	1,120	9.0	1.2	84
3	Etowah River at Rome, Georgia	02396000	1,820	13	1.2	81
4	Coosa River near Rome, Georgia	02397000	4,040	13	1.2	81
5	Alabama River near Montgomery, Alabama	02420000	15,087	16	.85	77
6	Cahaba River near Mountain Brook, Alabama	02423380	140	8.1	1.5	87
7	Little Cahaba River near Jefferson Park, Alabama	02423400	24.4	18	5.1	68
8	Cahaba River at Centreville, Alabama	02424000	1,027	10	1.2	81
9	Alabama River at Claiborne, Alabama	02429500	21,967	17	.58	74
10	Tombigbee River near Fulton, Mississippi	02431000	612	25	.31	61
11	Tibbee Creek near Tibbee, Mississippi	02441000	926	42	.19	46
12	Luxapallila Creek near Columbus, Mississippi	02443500	715	16	.25	72
13	Noxubee River near Geiger, Alabama	02448500	1,097	27	.36	57
14	Tombigbee River at Gainesville, Alabama	02449000	8,632	29	1.0	56
15	Sipsey Fork near Grayson, Alabama	02450250	92.1	1.5	.05	98
16	North River near Samantha, Alabama	02464000	223	10	.12	85
17	Black Warrior River below Seldon Lock and Dam near Eutaw, Alabama	02466031	5,810	15	1.2	76
18	Tombigbee River below Coffeeville Lock and Dam near Coffeeville, Alabama	02469762	18,417	22	.65	64

*USGS station number is based on geographic location and the downstream order of streamflow sites.

where A is the atmospheric deposition of nutrients, F is the fertilizer application of nutrients, C is the crop nitrogen fixation, P is the point source effluent nutrients, L is the instream nutrient load, H is the crop harvest (removal of nutrients), and S is the storage and processing of nutrients.

Other potential nutrient sources that have not been considered in this analysis include natural ground water inflow, storm water washoff, and septic tank discharge. Estimation of the source terms for this analysis has been limited to inputs that can be associated with available long term basin agricultural, point source, and atmospheric monitoring data. This association allows a limited evaluation of source trends.

Transformation processes were not considered in the mass balance. The output storage term (S in Equation 1) accounts for the storage and processing of nutrients in the basin. Accumulation and cycling of nutrients and loss of reactive nitrogen to the system by denitrification are particularly important elements of the storage term (Galloway *et al.*, 2003).

Correlation analysis was used to associate the basin nutrient yields and concentrations with land use. This test provides a means to assess which human land altering activities are associated with instream nutrient impacts. The mass balance

highlights the tremendous nutrient inputs from agriculture and other activities. The correlation analysis tests if instream nutrient levels are related to these activities.

One of the most difficult questions to answer in environmental assessment is "Is the water quality getting better or worse?" An evaluation of long term (decadal) trends in water quality for sites with sufficient long term data (1970 to 1997) gives a historical framework to help address this question. Multiple regression analysis was used to relate short term (annual) variation in instream nutrient concentrations and annual variation in agricultural input sources.

NUTRIENT INPUTS

Estimates of the total mass of nutrients entering each of the 18 subbasins were made by accounting for atmospheric deposition, fertilizer use, nitrogen fixation by agricultural crops, farm animal waste, and point-source inputs. Other sources, including naturally occurring mineralization, ground water inputs, effluent from septic tank systems, and nonfarm animal waste, were not accounted for in this analysis.

Atmospheric Deposition

Atmospheric nutrient inputs to the drainage subbasins were based on values from the Mobile River Basin as reported by Meyers *et al.* (2001). According to the Meyers study, estimated total annual nitrogen deposition in 42 coastal estuaries and their basins in the United States ranged from 0.86 to 4.0 tons per square mile per year ($\text{tons}/\text{mi}^2/\text{yr}$). The analysis was based on results of the U.S. Environmental Protection Agency's (USEPA) Regional Acid Deposition Model and field measurements from the USEPA's Clean Air Status and Trends Network (CASTNET) (Clarke *et al.*, 1997).

The total nitrogen input estimate of 2.34 tons/ mi^2/yr) used in this study for Mobile Bay was based on 1989 to 1996 data. Wet deposition composed 66 percent of the total nitrogen, and dry deposition composed 34 percent of the nitrogen input. Meyers *et al.* (2001) reported an increasing trend (1985 to 1996) in annual wet deposition of both nitrate and ammonium at the Sand Mountain Experimental Station in the Mobile River Basin (AL99, Figure 1). The nitrate increase was approximately 0.14 tons/ mi^2/yr and the ammonium increase was 0.06 tons/ mi^2/yr .

The primary anthropogenic sources of atmospheric nitrogen include combustion and emissions from waste treatment. Combustion of fossil fuels in electrical power generation and automobiles also are important sources. Natural sources of atmospheric nitrogen include biological action in soil and wetlands.

To obtain load estimates of atmospheric nitrogen inputs in the individual study basins, the value of 2.34 tons/ mi^2/yr was multiplied by the basin area (Meyers *et al.*, 2001). However, an uncertainty factor of 2 was determined for the nitrogen estimates, suggesting that the estimate of atmospheric nitrogen input may range from 1.17 to 4.68 tons/ mi^2/yr . The total atmospheric nitrogen input estimates for the Mobile River subbasins are given in Table 2.

The total phosphorus component of atmospheric nutrient loads was based on a literature derived value of 0.19 tons of total phosphorus deposited per square mile of drainage basin per year (McMahon and Woodside, 1997). Sources of atmospheric phosphorus are poorly understood. A principal source of atmospheric phosphorus is reentrained particulate material from soil. The 0.19 tons/ mi^2/yr value is based on a review of studies of atmospheric phosphorus inputs in the Albemarle-Pamlico estuary of North Carolina. Estimates of total phosphorus input in the Mobile River subbasins are given in Table 3.

Fertilizer

Chemical fertilizer applied on farmlands and residential lawns is an important source of nutrients in the Mobile River Basin. To estimate fertilizer nitrogen and phosphorus inputs, county sales data were apportioned to each subbasin by using the percentage of total agricultural area in the basin area of each county relative to the total agricultural area in the county. Use of fertilizer sales data to estimate inputs has been reported to give higher values than estimates based on fertilizer application rates recommended by agricultural research agencies (Harned *et al.*, 1995).

Fertilizer sales data were obtained from the Association of American Plant Food Control Officials at the University of Kentucky (David Lorenz, written communication, 1999). The accuracy of the county level estimates of fertilizer use depends, in part, on the movement of fertilizer sold from one county to a different county and other variables of accounting. These estimates are most suitable for analysis at the county scale and larger.

No clear trends in annual fertilizer sales were evident from 1990 to 1998 at the Tombigbee River (Site 18; Figure 2) or the Alabama River (Site 9; Figure 2), the farthest downstream stations in the Mobile River. The estimates of nutrient input from fertilizer commonly vary 25 percent or more per year.

The greatest mean nitrogen input during 1990 to 1998 (3.9 tons/ mi^2/yr) was in the Tibbee Creek Subbasin (Site 11, Table 2). The Tibbee Creek Subbasin has the highest amount of agricultural land in row crops (21.0 percent) and pasture (20.6 percent) of all the study subbasins. The lowest mean nitrogen input (0.1 tons/ mi^2/yr) from fertilizer was in Sipsey Fork (Site 15, Table 2), which is 98 percent forested.

The mean 1990 to 1998 total phosphorus input estimates from fertilizer indicate a similar pattern as the nitrogen inputs (Table 3; Figure 2). The greatest mean phosphorus input (0.96 tons/ mi^2/yr) was in the Tibbee Creek Subbasin (Site 11), and the least (0.02 tons/ mi^2/yr) was in the Sipsey Fork Subbasin (Site 15).

Nitrogen Fixation

Biologically fixed nitrogen produced by legumes, including peanuts and soybeans, is an important source of nitrogen in agricultural basins. Although soybeans are grown extensively in the Mobile River Basin, relatively small amounts of acreage are used to grow peanuts.

TABLE 2. Estimated Inputs and Outputs of Total Nitrogen in 18 Subbasins of the Mobile River Basin [(tons/mi²)/yr, tons per square mile per year; -, no data].

Map No. (Figure 1)	Station Name	Point Source	Atmospheric Input (tons/ mi ² /yr)	Mean Fertilizer Input 1990 to 1998 (tons/ mi ² /yr)	Nitrogen Fixation Input (tons/ mi ² /yr)	Animal Waste Input, 1997 (tons/ mi ² /yr)	Total Inputs (tons/ mi ² /yr)	Crop Removal Output, 1990 to 1998 (tons/ mi ² /yr)		Mean Instream Yield (tons/ mi ² /yr)	Storage (tons/ mi ² /yr)
								Crop Removal Output, 1990 to 1998 (tons/ mi ² /yr)	Total Inputs (tons/ mi ² /yr)		
1	Etowah River at Canton, Georgia		0.0050	2.3	.19	0.007	2.9	5.5	0.052	0.74	4.7
2	Etowah River at Allatoona Dam above Cartersville, Georgia	.14	2.3	.22	.010	.85	3.6	.013	-	-	-
3	Etowah River at Rome, Georgia	.19	2.3	1.1	.20	1.3	5.1	.27	-	-	-
4	Coosa River near Rome, Georgia	.18	2.3	.67	.36	3.4	7.0	.51	-	-	-
5	Alabama River near Montgomery, Alabama	.14	2.3	1.2	.14	2.7	6.7	.22	1.2	5.3	
6	Cahaba River near Mountain Brook, Alabama	.33	2.3	.60	0	1.2	4.4	.00024	2.0	2.4	
7	Little Cahaba River near Jefferson Park, Alabama	.66	2.3	1.6	0	3.2	7.9	.0017	1.9	6.0	
8	Cahaba River at Centreville, Alabama	.41	2.3	.86	.003	1.8	5.4	.023	1.2	4.1	
9	Alabama River at Claiborne, Alabama	.17	2.3	1.1	.22	3.7	7.6	.34	1.0	6.2	
10	Tombigbee River near Fulton, Mississippi	.021	2.3	1.7	2.0	2.4	8.5	2.1	1.2	5.1	
11	Tibbee Creek near Tibbee, Mississippi	.024	2.3	3.9	1.8	5.1	13	1.9	2.6	8.6	
12	Luxapallila Creek near Columbus, Mississippi	.037	2.3	1.3	.39	2.5	6.6	.58	2.2	3.8	
13	Noxubee River near Geiger, Alabama	.044	2.3	1.7	1.1	2.9	8.0	1.6	1.4	5.0	
14	Tombigbee River at Gainesville, Alabama	.035	2.3	1.9	1.4	3.7	9.4	1.7	-	-	
15	Sipsey Fork near Grayson, Alabama	0	2.3	.11	.010	.51	3.0	.020	2.0	.98	
16	North River near Samantha, Alabama	.056	2.3	1.4	.10	1.7	5.6	.26	.91	4.4	
17	Black Warrior River below Seldon Lock and Dam near Eutaw, Alabama	.26	2.3	1.4	.12	4.7	8.8	.21	1.6	7.0	
18	Tombigbee River below Coffeeville Lock and Dam near Coffeeville, Alabama	.11	2.3	1.4	.64	3.6	8.1	.80	1.3	6.0	

TABLE 3. Estimated Inputs and Outputs of Total Phosphorus in 18 Subbasins of the Mobile River Basin [(tons/mi²)/yr, tons per square mile per year; -, no data].

Map No. (Figure 1)	Station Name	Mean						Crop Removal		
		Point Source Input (tons/ mi ² /yr)	Atmospheric Input (tons/ mi ² /yr)	Fertilizer Input 1990 to 1998 (tons/ mi ² /yr)	Animal Waste Input, 1997 (tons/ mi ² /yr)	Total Inputs 1998 (tons/ mi ² /yr)	Crop Removal Output, 1990 to 1998 (tons/ mi ² /yr)	Mean Instream Yield (tons/ mi ² /yr)	Storage (tons/ mi ² /yr)	
1	Etowah River at Canton, Georgia	0.0020	0.19	0.047	0.42	0.66	0.0080	0.24	0.41	
2	Etowah River at Allatoona Dam above Cartersville, Georgia	.022	.19	.11	.16	.48	.0020	.13	.35	
3	Etowah River at Rome, Georgia	.15	.19	.18	.16	.67	.034	.20	.43	
4	Coosa River near Rome, Georgia	.091	.19	.14	.41	.83	.064	.29	.48	
5	Alabama River near Montgomery, Alabama	.036	.19	.21	.33	.76	.028	.084	.64	
6	Cahaba River near Mountain Brook, Alabama	.055	.19	.11	.20	.55	0	.18	.37	
7	Little Cahaba River near Jefferson Park, Alabama	.017	.19	.31	.48	.99	0	—	—	
8	Cahaba River at Centreville, Alabama	.12	.19	.15	.25	.70	.0040	.15	.54	
9	Alabama River at Claiborne, Alabama	.051	.19	.19	.46	.89	.044	.13	.71	
10	Tombigbee River near Fulton, Mississippi	.0070	.19	.43	.35	.97	.22	.18	.57	
11	Tibbee Creek near Tibbee, Mississippi	.0090	.19	.96	.74	1.9	.21	.25	1.4	
12	Luxapallila Creek near Columbus, Mississippi	.014	.19	.27	.27	.74	.073	.071	.60	
13	Noxubee River near Geiger, Alabama	.027	.19	.36	.42	1.0	.19	.30	.50	
14	Tombigbee River at Gainesville, Alabama	.021	.19	.41	.50	1.1	.19	—	—	
15	Sipsey Fork near Grayson, Alabama	0	.19	.023	.051	.26	.0030	.037	.22	
16	North River near Samantha, Alabama	.021	.19	.24	.18	.63	.037	.091	.50	
17	Black Warrior River below Seldon Lock and Dam near Eutaw, Alabama	.047	.19	.24	.51	.97	.028	.12	.82	
18	Tombigbee River below Coffeeville Lock and Dam near Cofeeville, Alabama	.027	.19	.26	.45	.93	.094	.20	.63	

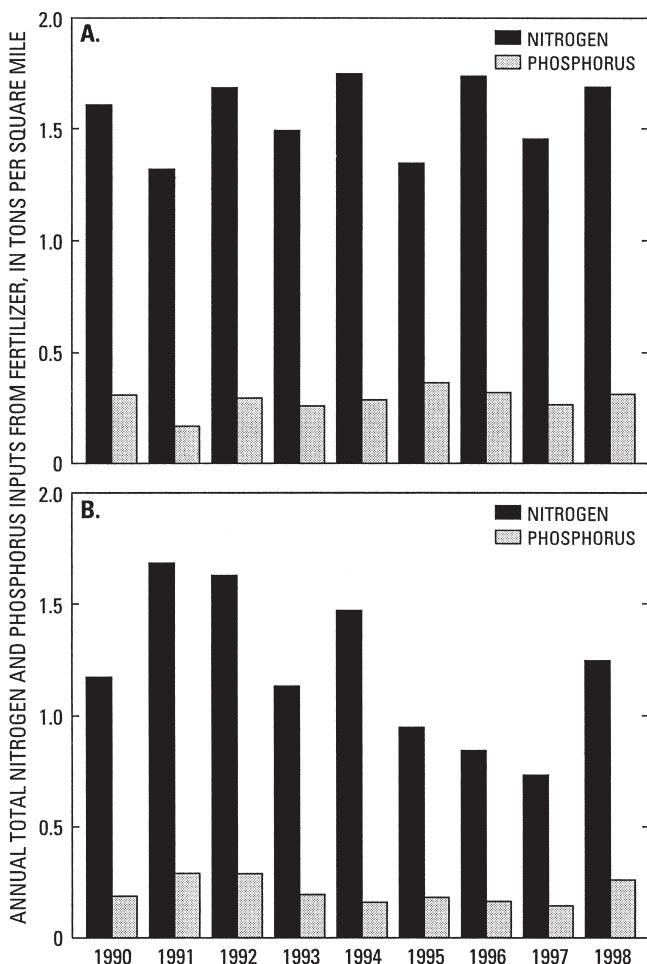


Figure 2. Annual Total Nitrogen and Phosphorus Inputs From Fertilizer for the (A) Tombigbee River (Site 18) and (B) Alabama River (Site 9).

The quantity of biologically fixed nitrogen produced by soybeans and peanuts was estimated by using the areal nitrogen fixation rate reported by Craig and Kuenzler (1983), and mean soybean and peanut crop production for 1990 to 1996 (Alabama Agricultural Statistics Service, 1996; Georgia Agricultural Statistics Service, 1996; Mississippi Agricultural Statistics Service, 1996). Craig and Kuenzler cite a nitrogen fixation rate of 33.6 tons/mi² for soybeans and 35.8 tons/mi² for peanuts. Annual variation in biologically fixed nitrogen is a function of annual legume acreage. Although the uncertainty in the estimation method is unknown, use of the mean value for seven crop years should be reasonable.

Estimates of nitrogen inputs from nitrogen fixation in each subbasin primarily reflect the amount of soybean acreage in the subbasin (Table 2). The highest inputs from nitrogen fixation occurred in the Tombigbee River (Site 10; 2.0 tons/mi²/yr, Table 2) and in

Tibbee Creek (Site 11; 1.8 tons/mi²/yr), both of which have high amounts of agricultural land use. Several subbasins, including Cahaba River (Site 6) and Little Cahaba River (Site 7), had no reported soybean or peanut agriculture. The nitrogen fixation input estimates for these two subbasins were set to zero.

Animal Waste

Fecal waste from cattle, hogs, chickens, turkeys, sheep, and horses represents a principal source of nitrogen and phosphorus in the Mobile River Basin. County level animal inventories were obtained for 1982, 1987, 1992, and 1997 from the Agricultural Statistics Service agencies of Alabama, Georgia, and Mississippi (Alabama Agricultural Statistics Service, 1996; Georgia Agricultural Statistics Service, 1996; Mississippi Agricultural Statistics Service, 1996). Animal counts were apportioned based on basin area relative to the number of total animals reported for each county in the subbasin.

To obtain estimates of nutrient input, literature-based values (Barker, 1991) of the nutrient content of animal waste were used in combination with the subbasin animal counts. The estimate for 1997 was used in the mass balance. Increasing trends in nutrient inputs from animal waste are apparent for most of the subbasins from 1982 to 1997. For example, the increase in estimated nutrient inputs from 1992 to 1997 in the Tombigbee River (Site 18; Figure 3A) and the Alabama River (Site 9; Figure 3B) is primarily the result of an increase in cattle production during the same period.

The 1997 estimates of total nitrogen input from animal waste (Table 2) were highest at Tibbee Creek (Site 11; 5.1 tons/mi²/yr), the Black Warrior River (Site 17; 4.7 tons/mi²/yr), the Alabama River (site 9; 3.7 tons/mi²/yr), and the Tombigbee River (Site 14; 3.7 tons/mi²/yr), all subbasins with particularly large populations of cattle and chickens. The lowest estimate was for the predominantly forested Sipsey Fork (Site 15; 0.51 tons/mi²/yr).

The 1997 estimates of total phosphorus inputs from animal waste (Table 3) indicate a similar pattern as for nitrogen inputs. Tibbee Creek (Site 11; 0.74 tons/mi²/yr), Black Warrior River (Site 17; 0.51 tons/mi²/yr), and Tombigbee River (Site 14; 0.50 tons/mi²/yr) had the highest estimated phosphorus inputs from animal waste. Sipsey Fork (Site 15), a predominantly forested subbasin, had the lowest estimated phosphorus input (0.05 tons/mi²/yr).

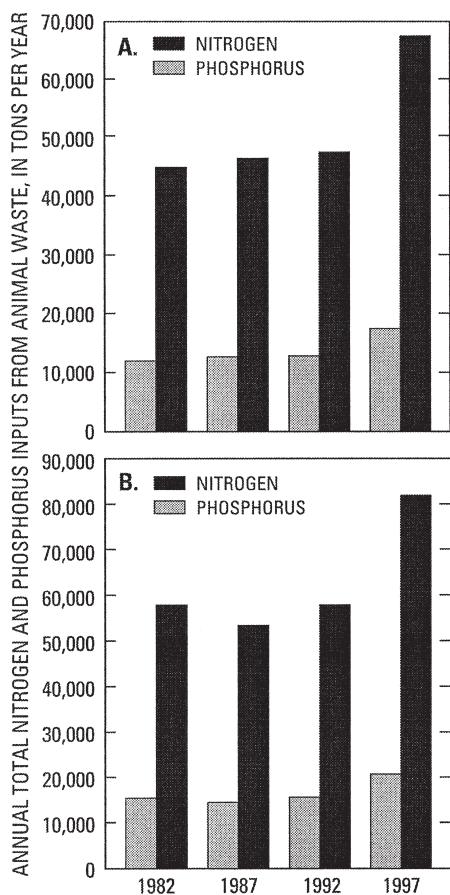


Figure 3. Annual Total Nitrogen and Phosphorus Inputs From Animal Waste for the (A) Tombigbee River (Site 18) and (B) Alabama River (Site 9).

Point Sources

Available point source location, discharge, and water quality data from the three states included in the Mobile River Basin were used to estimate nutrient inputs generated by discharges (Lynn Sisk, Alabama Department of Environmental Management, written communication, March 2, 2000; Mildred Granderson, Georgia Department of Natural Resources, written communication, August 9, 2000; Jo Sharpe, Mississippi Department of Environmental Quality, written communication, August 4, 2000). Data from Alabama included the 1997 to 1999 calendar years; data from Georgia included the 1997 to 1998 calendar years, and data from Mississippi included the 1997 to 2000 calendar years. Available daily discharge data and nutrient concentration data were compiled for 394 point sources in the Mobile River Basin. Not all of the sources had complete data. Where location data were absent, the USGS geographic names query system was used to identify

latitude and longitude. When discharge or effluent nutrient concentration data were missing, median values were used. Nitrogen effluent concentrations were not available for Georgia, so estimates of nitrogen concentrations were made by using a regression model developed from Alabama phosphorus and nitrogen concentration and flow data. In the resultant model relating Alabama phosphorus load and discharge to nitrogen load,

$$NL = -54.0 + 71.4(Q) + 0.6(PL) \quad (2)$$

where NL is point source nitrogen load estimate, in pounds per day; Q is point source discharge, in million gallons per day; and PL is point source phosphorus load, in pounds per day.

The coefficient of determination ($R^2 = 0.82$) and both point source discharge (Q) and phosphorus load (PL) were significantly linearly related to nitrogen load (NL) ($\alpha = 0.05$). To estimate the nitrogen load for Georgia point sources, the Q and PL terms in the model were replaced with Georgia values to predict NL.

An evaluation of change with respect to time in effluent discharges and concentrations is not possible using available data. However, data based estimates were compared with the Resources for the Future (RFF) Point Source Inventory (Gianessi and Peskin, 1984), in which 1977 to 1981 nationwide discharge data were evaluated to provide a check for the current study (1997 to 2000) estimates. The RFF county level point source discharge estimates were apportioned for each subbasin by using the percentage of total basin area in the county relative to the total area of the county.

In general, the 1977 to 1981 RFF point-source estimates are considerably higher than those for the current study (Table 4). The mean 1997 to 2000 nitrogen point source estimate is only 32 percent of the RFF estimate, and the mean 1997 to 2000 phosphorus point source estimate is 55 percent of the RFF value (Table 4). This difference reflects the uncertainty inherent in point source accounting exercises, different methodologies used in the estimation process, the inadequacy of available point source discharge and concentration data, and possibly a reduction in point source discharges into the Mobile River Basin between the years 1977 and 2000.

Analysis of seasonality in the 1997 to 1999 point source data for Alabama indicates that median monthly effluent discharges were highest in winter months and lowest in summer and early fall (Figure 4A). This pattern also is reflected in the median monthly ammonia, nitrate, and phosphorus point source loads (Figures 4B, 4C, and 4D).

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TABLE 4. Point Source Inputs Estimated From the Current Study (CS) and Resources for the Future (RFF) Point Source Inventory (Gianessi and Peskin, 1984) [(tons/mi²)/yr, tons per square mile per year; –, no data].

Map No. (Figure 1)	Station Name	No. of Sources	Discharge (Mgal/yr)	Point Source Input				CS/RFF Percent	
				RFF	Nitrogen (tons/mi ² /yr) CS	Phosphorus (ton/mi ² /yr) RFF	CS		
1	Etowah River at Canton, Georgia	3	136	0.45	0.0051	1.1	0.011	0.0020	18
2	Etowah River at Allatoona Dam above Cartersville, Georgia	9	6,470	1.1	.14	13	.27	.022	8.1
3	Etowah River at Rome, Georgia	13	9,290	.36	.19	53	.053	.15	280
4	Coosa River near Rome, Georgia	39	22,600	1.4	.18	13	.28	.091	32
5	Alabama River near Montgomery, Alabama	80	66,300	.35	.14	40	.063	.038	60
6	Cahaba River near Mountain Brook, Alabama	3	1,930	2.1	.33	16	.34	.056	16
7	Little Cahaba River near Jefferson Park, Alabama	1	657	2.5	.66	26	.41	.017	4.1
8	Cahaba River at Centreville, Alabama	15	12,400	.95	.41	43	.16	.12	75
9	Alabama River at Claiborne, Alabama	146	114,000	.54	.17	31	.10	.051	51
10	Tombigbee River near Fulton, Mississippi	6	1,061	.071	.020	28	.045	.0071	16
11	Tibbee Creek near Tibbee, Mississippi	15	1,830	.16	.024	15	.061	.0086	14
12	Luxapallila Creek near Columbus, Mississippi	8	1,290	.080	.037	46	.020	.014	70
13	Noxubee River near Geiger, Alabama	20	4,024	.050	.044	88	.027	.027	100
14	Tombigbee River at Gainesville, Alabama	197	22,800	.15	.035	23	.060	.021	35
15	Sipsey Fork near Grayson, Alabama	0	0	.0030	0	–	.00072	0	–
16	North River near Samantha, Alabama	1	580	.080	.056	70	.017	.021	120
17	Black Warrior River below Seldon Lock and Dam near Eutaw, Alabama	29	54,600	.57	.26	46	.11	.047	43
18	Tombigbee River below Coffeeville Lock and Dam near Coffeeville, Alabama	248	82,700	.26	.11	42	.062	.027	44
Mean						32			55

Point source data estimates for nitrogen (Table 2) indicate that the highest inputs occurred in the Little Cahaba River near Jefferson Park (Site 7; 0.66 tons/mi²/yr), Cahaba River at Centreville (Site 8; 0.41 tons/mi²/yr), Cahaba River near Mountain Brook (Site 6; 0.33 tons/mi²/yr), and Black Warrior River (Site 17; 0.26 tons/mi²/yr). Sipsey Fork (Site 15) had no point source nitrogen inputs.

Point source data estimates for phosphorus (Table 3) indicate that the highest inputs occurred in the Etowah River (Site 3; 0.15 tons/mi²/yr), Cahaba River at Centreville (Site 8; 0.12 tons/mi²/yr), and Cahaba River near Mountain Brook (Site 6; 0.06 tons/mi²/yr). No point source phosphorus inputs were reported for Sipsey Fork (Site 15).

NUTRIENT OUTPUTS

Estimates of the total mass of nutrients leaving each of the 18 subbasins were made by calculating the amount of nutrients removed by crop harvest and instream nutrient loads. Crop harvest nutrient removal during 1990 to 1998 was estimated for each subbasin from county crop acreage data and literature based crop nutrient content estimates. Instream nutrient loads represent the total mass of total nitrogen or total phosphorus transported by a stream. Annual instream loads were calculated for each gaging station for all years for which sufficient discharge and water quality data were available. A nutrient

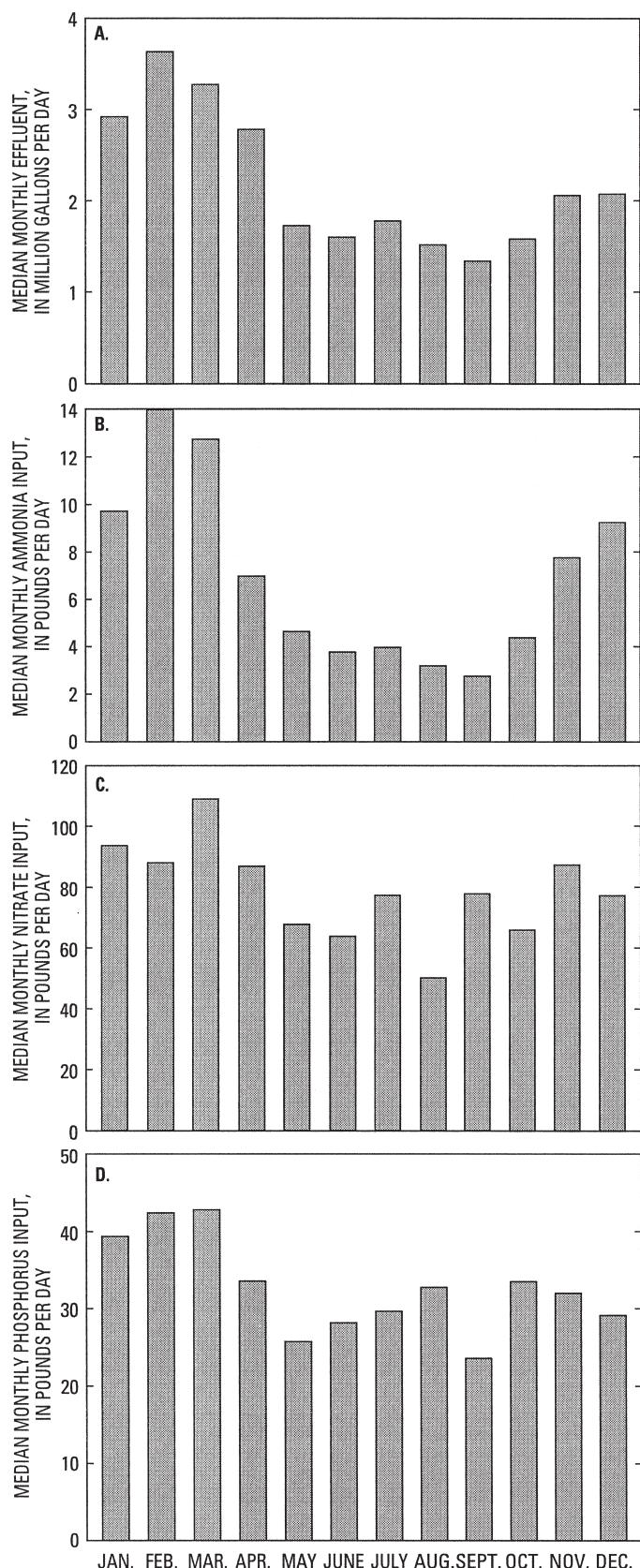


Figure 4. Seasonality in Monthly Median Daily Point Source Loads in the Mobile River Basin in Alabama for (A) Effluents, (B) Ammonia, (C) Nitrate, and (D) Phosphorus.

storage estimate was calculated by subtracting the estimate of the total mass of nutrient outputs from the estimate of the total mass of nutrient inputs in each subbasin.

Crop Harvest

Crop harvest is a quantifiable mechanism for removal of nutrients from a basin. The assumption used in this accounting exercise is that the crop harvest nutrients are indeed removed from the basin or converted to a form that is accounted for by another major category of the mass balance, such as animal waste or point source effluent (human waste).

Estimates of crop related nutrient removal from the Mobile River subbasins were made by using annual county crop-harvest data reported by the Agricultural Statistics Service agencies of Alabama, Georgia, and Mississippi (Alabama Agricultural Statistics Service, 1996; Georgia Agricultural Statistics Service, 1996; Mississippi Agricultural Statistics Service, 1996). County crop harvest data were apportioned to each subbasin by using the percentage of total basin agricultural area in the county relative to the total agricultural area in the county.

To obtain estimates of nutrient removal, literature-based estimates of the nutrient content of crop materials were used in conjunction with the basin crop harvest estimates. Year to year changes in nutrient removal by crop harvest reflect trends in agriculture, including economic, climatic, and management based variability. Trends in nitrogen and phosphorus removal by crop harvest are virtually identical. Cultivation of corn and soybeans has produced the largest harvests in the basin over the past 30 years and, therefore, account for much of the nutrient removal by crop harvest. A distinct basinwide pattern in the long term trends of nitrogen removal is evident. Soybean harvests, and the corresponding nitrogen removal, increased until about 1980 and then decreased from 1980 to 1997. The inverse of this trend occurred for corn harvest and nitrogen removal. An example of these trends, which are evident at most of the Mobile River subbasins, is shown in Figure 5 for the Tombigbee River (Site 18). Except for several of the small subbasins with few agricultural land uses where row cropping has almost disappeared entirely, corn has replaced soybeans as the primary harvested crop in the basin over the last 20 years.

The mean 1990 to 1998 total nitrogen output estimates from crop harvest indicate the amount of agriculture in each subbasin of the Mobile River Basin (Table 2). The highest yields include the Tombigbee River (Site 10; 2.1 tons/mi²/yr) and Tibbee Creek (Site 11; 1.9 tons/mi²/yr), both of which are extensively

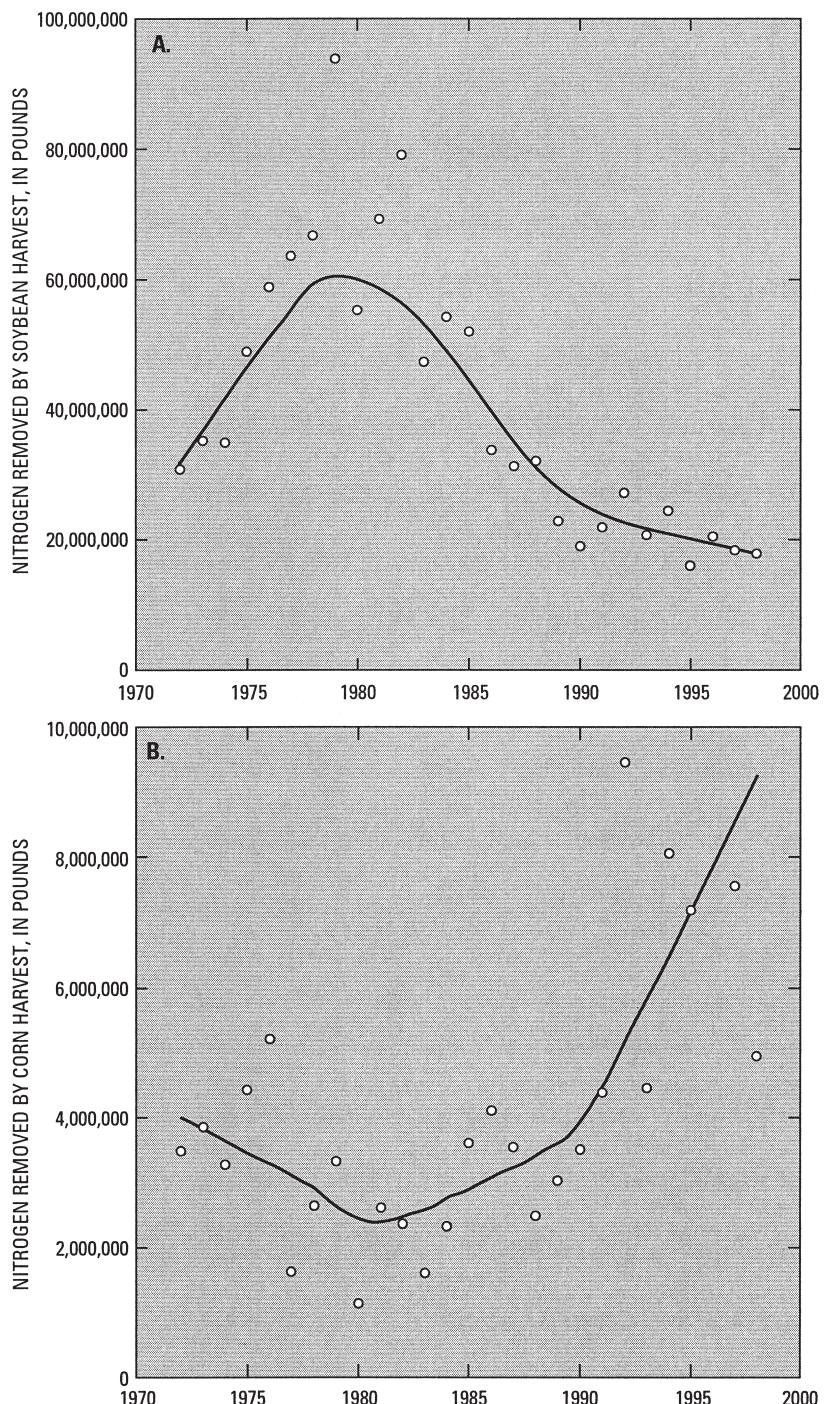


Figure 5. Nitrogen Removal by Annual Harvests of (A) Soybean and (B) Corn in the Tombigbee River (Site 18) Subbasin.

farmed areas. The lowest yields include the Cahaba River (Site 6; 0.00024 tons/mi²/yr) and the Little Cahaba River (Site 7; 0.0017 tons/mi²/yr), which are subbasins with little agriculture. The mean 1990 to 1998 total phosphorus output estimates from crop harvest in the Mobile River subbasins (Table 3) have similar patterns to those for nitrogen.

Instream Loads

Annual instream loads of nitrogen and phosphorus were calculated as the product of the daily streamflow and estimated daily concentrations in the 18 subbasins. The estimates of daily nitrogen and phosphorus concentrations were obtained by using a

five-variable log linear regression model (Cohn *et al.*, 1989; Gilroy *et al.*, 1990; Cohn *et al.*, 1992):

$$\ln(c) = \beta_0 + \beta_1 \ln Q + \beta_2 t + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + e \quad (3)$$

where \ln is the natural logarithm function; c is the concentration, in milligrams per liter; Q is the instantaneous discharge at time of concentration sampling, in cubic feet per second; t is the time, in decimal years; \sin is the sine function; \cos is the cosine function; π is the 3.14169; β_0 to β_4 are the coefficients of the regression model; and e is the model error term.

The discharge term ($\beta_1 \ln Q$) in the model addresses variability in concentration resulting from discharge variability. The time term ($\beta_2 t$) adjusts for variability resulting from a linear time trend in concentration,

and the sine and cosine terms adjust for seasonal variability in concentration.

Bias generated in the estimated load when the load is transformed from log to linear units was corrected by using the minimum variance unbiased estimator correction (MVUE) (Bradu and Mundlak, 1970). Censored data were statistically adjusted by using the adjusted maximum likelihood estimator described by Cohn (1988).

Nitrogen loads (Table 5) and yields (Table 6) were estimated for 1988 to 1996 in the Mobile River subbasins. The mean total nitrogen loads estimated for the Tombigbee River (Site 18; Table 5; 24,000 tons/yr) and Alabama River (Site 9; 22,000 tons/yr) represent outputs from the most downstream locations examined and major inputs to the Mobile Bay estuarine system. The mean nitrogen yield for the Tombigbee

TABLE 5. Estimated Nitrogen Loads for the Mobile River Subbasins for 1988 to 1996 (–, no data; tons/yr, tons per year).

Map No. (Figure 1)	Station Name	Annual Nitrogen Load (tons/yr)										
		1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean	Median
1	Etowah River at Canton, Georgia	150	280	480	430	460	590	510	490	750	460	480
2	Etowah River at Allatoona Dam above Cartersville, Georgia	–	–	–	–	–	–	–	–	–	–	–
3	Etowah River at Rome, Georgia	–	–	–	–	–	–	–	–	–	–	–
4	Coosa River near Rome, Georgia	–	–	–	–	–	–	–	–	–	–	–
5	Alabama River near Montgomery, Alabama	7,100	19,000	27,000	–	–	–	–	–	–	18,000	19,000
6	Cahaba River near Mountain Brook, Alabama	310	240	180	280	260	230	410	310	–	280	270
7	Little Cahaba River near Jefferson Park, Alabama	21	49	51	41	31	52	47	45	68	45	47
8	Cahaba River at Centreville, Alabama	–	820	1,000	920	620	1,300	1,100	1,500	2,900	1,300	1,100
9	Alabama River at Claiborne, Alabama	9,200	24,000	32,000	20,000	18,000	26,000	21,000	19,000	28,000	22,000	21,000
10	Tombigbee River near Fulton, Mississippi	200	1,200	670	2,200	740	530	220	360	570	740	570
11	Tibbee Creek near Tibbee, Mississippi	650	2,500	1,900	5,100	1,200	2,000	3,000	3,100	2,400	2,400	2,400
12	Luxapallila Creek near Columbus, Mississippi	250	1,400	1,500	3,200	760	1,300	2,000	2,000	–	1,600	1,500
13	Noxubee River near Geiger, Alabama	280	2,300	2,100	3,500	540	1,500	1,300	1,300	1,200	1,600	1,300
15	Sipsey Fork near Grayson, Alabama	36	330	220	440	74	110	150	170	98	180	150
16	North River near Samantha, Alabama	55	320	290	350	110	170	180	160	180	200	180
17	Black Warrior River below Seldon Lock and Dam near Eutaw, Alabama	3,300	12,000	14,000	12,000	5,400	9,300	9,000	8,500	11,000	9,400	9,300
18	Tombigbee River below Coffeeville Lock and Dam near Coffeeville, Alabama	8,000	31,000	34,000	40,000	14,000	23,000	23,000	22,000	22,000	24,000	23,000

NUTRIENT MASS BALANCE AND TRENDS, MOBILE RIVER BASIN, ALABAMA, GEORGIA, AND MISSISSIPPI

TABLE 6. Estimated Nitrogen Yields for the Mobile River Subbasins for 1988 to 1996
[mi², square miles; tons/mi²/yr, tons per square mile per year; -, no data].

Map No. (Figure 1)	Station	Drainage Area (mi ²)	Nitrogen Yield (ton/mi ² /yr)								
			1988	1989	1990	1991	1992	1993	1994	1995	1996
1	Etowah River at Canton, Georgia	613	0.25	0.45	0.77	0.70	0.74	0.95	0.82	0.79	1.2
2	Etowah River at Allatoona Dam above Cartersville, Georgia	1,120	-	-	-	-	-	-	-	-	-
3	Etowah River at Rome, Georgia	1,820	-	-	-	-	-	-	-	-	-
4	Coosa River near Rome, Georgia	4,040	-	-	-	-	-	-	-	-	-
5	Alabama River near Montgomery, Alabama	15,087	.47	1.3	1.8	-	-	-	-	-	1.2
6	Cahaba River near Mountain Brook, Alabama	140	2.2	1.7	1.3	2.0	1.9	1.6	2.9	2.2	-
7	Little Cahaba River near Jefferson Park, Alabama	24.4	.84	2.0	2.1	1.7	1.3	2.1	2.0	1.9	2.0
8	Cahaba River at Centreville, Alabama	1,027	-	.80	.97	.89	.61	1.3	1.1	1.5	2.8
9	Alabama River at Claiborne, Alabama	21,967	.42	1.1	1.5	.91	.81	1.2	.93	.84	1.3
10	Tombigbee River near Fulton, Mississippi	612	.33	2.0	1.1	3.7	1.2	.86	.36	.59	.93
11	Tibbee Creek near Tibbee, Mississippi	926	.70	2.7	2.0	5.5	1.3	2.1	3.2	3.3	2.5
12	Luxapallila Creek near Columbus, Mississippi	715	.35	2.0	2.1	4.5	1.1	1.8	2.7	2.8	-
13	Noxubee River near Geiger, Alabama	1,097	.25	2.1	1.9	3.2	.50	1.4	1.2	1.2	1.4
15	Sipsey Fork near Grayson, Alabama	92.1	.39	3.6	2.4	4.8	.80	1.2	1.6	1.9	1.1
16	North River near Samantha, Alabama	223	.25	1.5	1.3	1.6	.48	.76	.83	.71	.81
17	Black Warrior River below Seldon Lock and Dam near Eutaw, Alabama	5,810	.57	2.0	2.4	2.1	.92	1.6	1.6	1.5	1.9
18	Tombigbee River below Coffeeville Lock and Dam near Coffeeville, Alabama	18,417	.44	1.7	1.9	2.2	.74	1.2	1.2	1.2	1.3

River (Site 18; Tables 2, 6; 1.3 tons/mi²/yr), which drains a greater percentage of agricultural (row crop) land use, was greater than the mean nitrogen yield for the Alabama River (Site 9; 1.0 tons/mi²/yr).

Two headwater tributaries to the Tombigbee River had the highest estimated mean total nitrogen yields – Tibbee Creek (Site 11; 2.6 tons/mi²/yr) and Luxapallila Creek (Site 12; 2.2 tons/mi²/yr). Other sites having comparatively elevated yields were the Cahaba River (Site 6; 2.0 tons/mi²/yr) and the Little Cahaba River (Site 7; 1.9 tons/mi²/yr), located in the Alabama River Subbasin, and Sipsey Fork (Site 15; 2.0 tons/mi²/yr) in the Black Warrior River Subbasin (Tables 2 and 6).

In a study conducted during 1972 to 1993, Dunn (1996) examined nutrient loads for 37 streams flowing into the Gulf of Mexico, including the Tombigbee and Alabama Rivers. A comparison of the mean annual total nitrogen yields for the 37 streams provides a frame of reference for the Mobile River subbasins. The mean annual nitrogen yield for the 37 streams was 1.7 tons/mi²/yr/yr (median is 1.0) – very close to the mean yield values estimated for the Tombigbee River (Site 18; 1.3 tons/mi²/yr) and the Alabama River (Site 9; 1.0 tons/mi²/yr). Compared with yields from other rivers flowing into the Gulf of Mexico, the Mobile River Basin nitrogen yields are close to the middle of the range of estimated yields.

Phosphorus loads and yields were estimated for the subbasins in the Mobile River Basin for 1988 to 1996 (Tables 7 and 8). Mean total phosphorus loads were estimated to be 3,200 tons/yr in the Tombigbee River (Site 18) and 2,400 tons/yr in the Alabama River (Site 9). The mean phosphorus yield for the Tombigbee River (Site 18; 0.20 tons/mi²/yr) was greater than the mean phosphorus yield for the Alabama River (Site 9; 0.13 tons/mi²/yr). The phosphorus yield for the Tombigbee River in the headwaters of the subbasin (Site 10; 0.18 tons/mi²/yr) was similar to the estimated phosphorus yield at the most downstream site, indicating little range in nutrient concentrations from the subbasin. The highest estimated mean phosphorus yield was for the Noxubee River (Site 13; 0.30 tons/mi²/yr), located in an agricultural area of the Tombigbee River Subbasin. The estimated mean phosphorus yield for Tibbee Creek (Site 11), another headwater tributary in an agricultural area of the Tombigbee River, was 0.25 tons/mi²/yr. Other comparatively elevated yields were estimated for the Etowah River at Rome (Site 3; 0.20 tons/mi²/yr), Etowah River at Canton (Site 1; 0.24 tons/mi²/yr), and the Coosa River (Site 4; 0.29 tons/mi²/yr). These two rivers drain developed areas around Rome, Georgia, and flow into Weiss Lake in Alabama (Figure 1), an impoundment of the Coosa River. Weiss Lake was

classified as eutrophic (Alabama Department of Environmental Management, 1996).

A comparison of phosphorus yield estimates for streams in the Dunn study (1996), similar to the nitrogen comparison, indicates that the phosphorus yields of the Tombigbee and Alabama Rivers are in the middle of the range of values for estimated phosphorus yields for streams draining into the Gulf of Mexico. The mean of the mean annual phosphorus yields for the 37 streams was 0.46 (ton/mi²)/yr (median = 0.10 tons/mi²/yr) compared to the Tombigbee River (Site 18) estimated mean yield of 0.20 tons/mi²/yr (Table 8) and the Alabama River (Site 9) estimated mean yield of 0.13 tons/mi²/yr.

MASS BALANCE DISCUSSION

A review of the relative percentages of nutrient-source inputs compared to outputs indicates the importance of agricultural nutrient inputs and the capacity of the basin to store and process nutrients. Although a great deal of uncertainty is involved in any mass balance accounting of this kind, the exercise highlights factors that influence the transport and fate of nitrogen and phosphorus in the Mobile River Basin.

Nitrogen

Nitrogen inputs from point sources, atmospheric deposition, crop fertilizer, animal waste, and biological nitrogen fixation expressed as percentages of total inputs were estimated for each of the 18 drainage subbasins (Table 9, Figure 6). Total nitrogen inputs ranged from 18 to 79 percent of the total nitrogen input from atmospheric deposition (38 percent mean), 17 to 54 percent from animal waste (37 percent mean), 4 to 30 percent from crop fertilizer (17 percent mean), 0 to 15 percent from biological nitrogen fixation (4 percent mean), and 0 to 8.4 percent from point sources (2.5 percent mean).

Nitrogen inputs from animal waste were the largest inputs in 12 of the 18 subbasins (Table 9), and the highest inputs indicate greater density of farm animals in the subbasins. Animal waste inputs in the Mobile River Basin (mean = 2.7 tons/mi²/yr, Table 2) are less than those reported for the Upper Potomac (5.8 tons/mi²/yr) (Jaworski *et al.*, 1992) and similar to those reported for the Albemarle-Pamlico Basin (2.9 tons/mi²/yr) (Stanley, 1989).

The second largest nitrogen input to the subbasins generally was from atmospheric deposition, which

TABLE 7. Estimated Phosphorus Loads for the Mobile River Subbasins for 1988 to 1996 (mi², square miles; tons/yr, tons per year).

Map No. (Figure 1)	Station	Drainage Area (mi ²)	Phosphorus Load (tons/yr)								
			1988	1989	1990	1991	1992	1993	1994	1995	1996
1	Etowah River at Canton, Georgia	613	26	83	230	100	45	140	93	77	200
2	Etowah River at Allatoona Dam above Cartersville, Georgia	1,120	27	65	200	110	96	160	94	91	190
3	Etowah River at Rome, Georgia	1,820	89	200	520	280	400	250	230	443	300
4	Coosa River near Rome, Georgia	4,040	440	960	1,500	1,000	900	1,100	920	830	1,200
5	Alabama River near Montgomery, Alabama	15,087	460	1,300	2,000	—	—	—	—	—	—
6	Cahaba River near Mountain Brook, Alabama	140	15	16	14	19	23	17	33	30	24
8	Cahaba River at Centreville, Alabama	1,027	—	—	171	120	60	120	91	110	171
9	Alabama River at Claiborne, Alabama	21,967	890	2,500	4,000	2,000	1,800	3,000	2,100	2,000	3,100
10	Tombigbee River near Fulton, Mississippi	612	15	160	73	360	150	47	22	33	42
11	Tibbee Creek near Tibbee, Mississippi	926	60	270	160	520	100	140	240	210	140
12	Luxapallila Creek near Columbus, Mississippi	715	8	58	56	130	21	33	51	49	—
13	Noxubee River near Geiger, Alabama	1,097	51	440	410	640	100	280	230	250	220
15	Sipsey Fork near Grayson, Alabama	92.1	1.0	4.5	3.7	5.6	1.6	2.3	2.8	2.9	2.5
16	North River near Samantha, Alabama	223	4.0	21	24	23	9.1	17	17	16	20
17	Black Warrior River below Seldon Lock and Dam near Eutaw, Alabama	5,810	140	710	930	810	270	570	550	530	780
18	Tombigbee River below Coffeeville Lock and Dam near Coffeeville, Alabama	18,417	720	4,100	5,000	5,900	1,500	2,930	3,000	3,000	2,900

TABLE 8. Estimated Phosphorus Yields for the Mobile River Subbasins for 1988 to 1996 [mi², square miles; tons/mi²/yr, tons per square mile per year].

Map No. (Figure 1)	Station	Drainage Area (mi ²)	Phosphorus Load (tons/mi ² /yr)								
			1988	1989	1990	1991	1992	1993	1994	1995	1996
1	Etowah River at Canton, Georgia	613	0.043	0.135	0.37	0.16	0.22	0.15	0.13	0.80	0.24
2	Etowah River at Allatoona Dam above Cartersville, Georgia	1,120	.024	.058	.18	.094	.086	.14	.084	.082	.42
3	Etowah River at Rome, Georgia	1,820	.049	.11	.28	.15	.22	.14	.13	.60	.20
4	Coosa River near Rome, Georgia	4,040	.11	.24	.36	.25	.22	.27	.23	.20	.72
5	Alabama River near Montgomery, Alabama	15,087	.031	.088	.13	—	—	—	—	.29	.24
6	Cahaba River near Mountain Brook, Alabama	140	.11	.11	.10	.14	.17	.12	.24	.22	.43
8	Cahaba River at Centreville, Alabama	1,027	—	—	.17	.12	.058	.12	.089	.11	.41
9	Alabama River at Claiborne, Alabama	21,967	.040	.12	.18	.093	.084	.14	.093	.090	.35
10	Tombigbee River near Fulton, Mississippi	612	.024	.27	.12	.59	.24	.077	.036	.054	.17
11	Tibbee Creek near Tibbee, Mississippi	926	.064	.29	.18	.56	.11	.15	.26	.23	.39
12	Luxapallila Creek near Columbus, Mississippi	715	.11	.082	.078	.18	.029	.046	.071	.069	—
13	Noxubee River near Geiger, Alabama	1,097	.046	.39	.37	.58	.093	.26	.21	.23	.51
15	Sipsey Fork near Grayson, Alabama	92.1	.0090	.049	.041	.061	.017	.024	.030	.032	.067
16	North River near Samantha, Alabama	223	.019	.095	.11	.11	.041	.074	.076	.073	.077
17	Black Warrior River below Seldon Lock and Dam near Eutaw, Alabama	5,810	.024	.12	.16	.14	.047	.098	.095	.091	.091
18	Tombigbee River below Coffeeville Lock and Dam near Coffeeville, Alabama	18,417	.039	.22	.27	.32	.080	.16	.16	.39	.20

NUTRIENT MASS BALANCE AND TRENDS, MOBILE RIVER BASIN, ALABAMA, GEORGIA, AND MISSISSIPPI

TABLE 9. Estimated Nitrogen Mass Balance as a Percentage of Total Inputs to the Mobile River Basin (–, no data).

Map No. (Figure 1)	Station Name	Point Source Input (percent)	Atmospheric Input (percent)	Mean Fertilizer Input 1990 to 1998 (percent)	Animal Waste Input, 1997 (percent)	Nitrogen Fixation Input, 1997 (percent)	Crop Removal Output 1990 to 1998 (percent)	Mean Instream Yield (percent)	Crop Storage (percent)
1	Etowah River at Canton, Georgia	0	42	4	54	0.1	0.44	14	85
2	Etowah River at Allatoona Dam above Cartersville, Georgia	4.0	66	6	24	.30	.36	–	–
3	Etowah River at Rome, Georgia	3.7	46	21	25	4.0	5.4	–	–
4	Coosa River near Rome, Georgia	2.6	34	10	49	5.2	7.3	–	–
5	Alabama River near Montgomery, Alabama	2.1	35	18	43	2.0	3.2	18	79
6	Cahaba River near Mountain Brook, Alabama	7.5	53	14	26	0	.0053	45	55
7	Little Cahaba River near Jefferson Park, Alabama	8.4	30	21	41	0	.022	24	76
8	Cahaba River at Centreville, Alabama	7.7	43	16	33	.056	.43	23	77
9	Alabama River at Claiborne, Alabama	2.3	31	15	49	2.9	4.5	13	82
10	Tombigbee River near Fulton, Mississippi	.25	28	20	29	2.4	25	15	61
11	Tibbee Creek near Tibbee, Mississippi	.18	18	30	39	13	15	20	66
12	Luxapallila Creek near Columbus, Mississippi	.56	36	20	38	6.0	8.9	33	58
13	Noxubee River near Geiger, Alabama	.54	29	21	35	14	20	18	63
14	Tombigbee River at Gainesville, Alabama	.37	24	20	40	15	18	–	–
15	Sipsey Fork near Grayson, Alabama	0	79	4	17	.34	.69	66	33
16	North River near Samantha, Alabama	.99	42	26	30	1.8	4.6	16	79
17	Black Warrior River below Seldon Lock and Dam near Eutaw, Alabama	3.0	27	16	53	1.3	2.4	18	79
18	Tombigbee River below Coffeeville Lock and Dam near Coffeeville, Alabama	1.3	29	17	45	7.9	9.8	16	74

was the greatest nitrogen source in six of the 18 subbasins (Table 9). A constant atmospheric nitrogen input value of 2.3 tons/mi² was used in this accounting (Table 2), which is lower than other reported regional atmospheric input values. For example, atmospheric total nitrogen input rates have been estimated at 3.5 tons/mi² for the Neuse, Tar-Pamlico, and Chowan river basins in North Carolina (Dodd *et al.*, 1992) and 4.1 tons/mi² for the Chesapeake Bay drainage (Fisher and Oppenheimer, 1991).

Data from the National Atmospheric Deposition Program (NADP) indicate that the highest national nitrate atmospheric inputs occur in the Northeast and Midwest of the United States. The primary sources of

these inputs are large coal burning powerplants and automobile emissions. Nitrogen inputs in the Mobile River Basin are near the middle of the range of national values. The fact that atmospheric inputs in the Mobile Basin are one of the dominant sources of nitrogen in an area of the country with mid-range nitrogen inputs highlights the importance of atmospheric inputs, but also is a result, to a lesser degree, of agricultural development in the basin compared to other basins draining large estuarine areas, such as the Chesapeake or Albemarle-Pamlico systems.

Fertilizer inputs are the third most important source of nitrogen in all but one of the 18 subbasins (4 to 30 percent of total inputs) and the second most

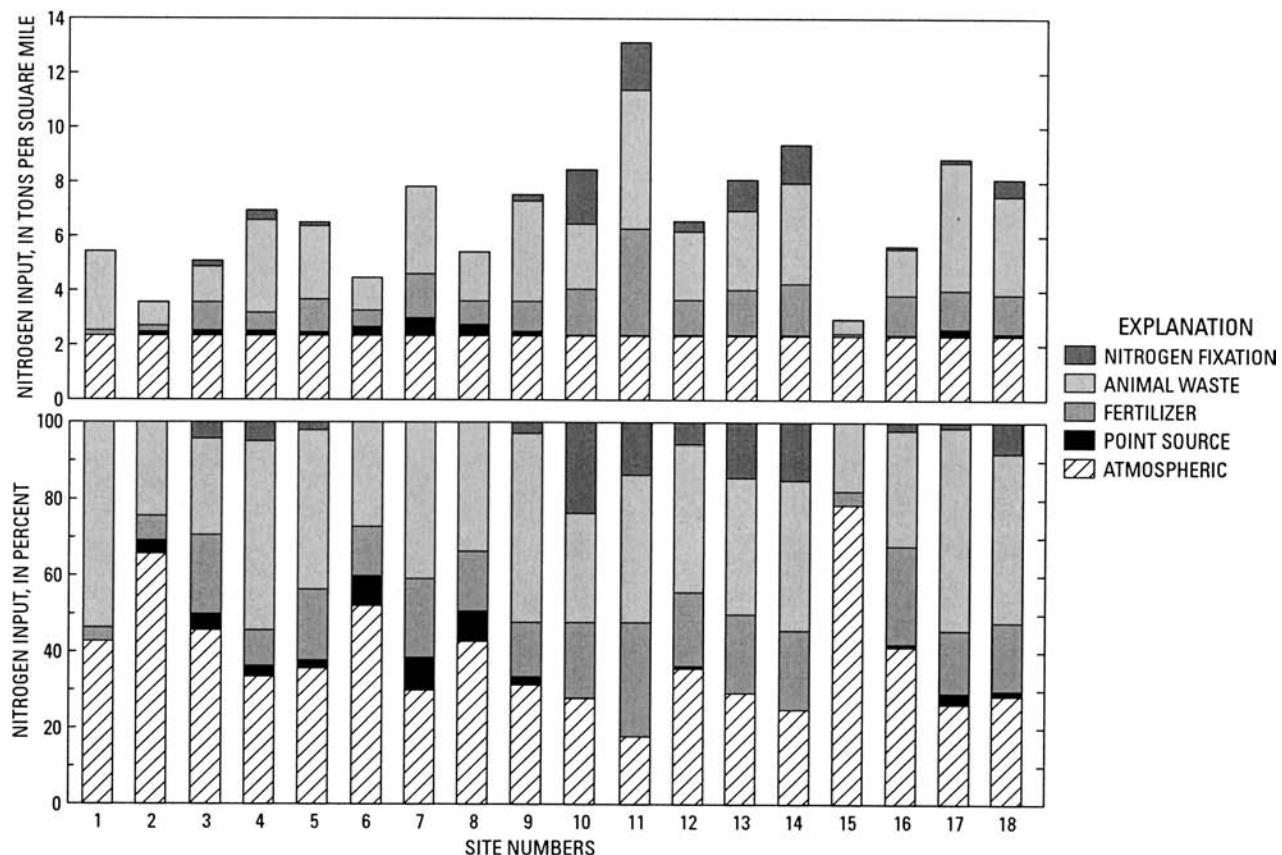


Figure 6. Nitrogen Inputs at Sites in the Mobile River Basin.

important source in Tibbee Creek (Site 11; 30 percent, Table 9). This stream is in the Tombigbee River Subbasin and drains an intensely agricultural area in Mississippi.

Crop related nitrogen fixation is the fourth most important source of nitrogen in 12 of the 18 subbasins (0.1 to 15 percent of total inputs, Table 9). The highest rates of biological nitrogen fixation were in the Tombigbee River (Site 14; 15 percent), the Noxubee River (Site 13; 14 percent), and Tibbee Creek (Site 11; 13 percent). These values represent higher proportions of soybean and legume crops in these subbasins than in the others.

Point source nitrogen contributions ranged from 0 at two sites to 8.4 percent of the total nitrogen inputs at the Little Cahaba River (Site 7; Table 9). The Cahaba River Subbasin includes much of the developed area around Birmingham, Alabama, and, therefore, has a relatively high density of point source inputs. The Cahaba River at Centreville (Site 8; 7.7 percent), the Cahaba River near Mountain Brook (Site 6; 7.5 percent), and the Etowah River (Site 2, 4 percent) had substantial inputs from point sources. These percentages and the associated input rates are

similar to point source contributions reported in other studies of large river basins.

Although the relative percentage of nitrogen input from point sources is small compared to the other input source categories, it is important to note that all point source nutrients are delivered directly to the stream. More than 30 percent of the instream nitrogen yield may be accounted for by point source inputs alone for the Little Cahaba River (Site 7; 34 percent) and for the Cahaba River at Centreville (Site 8; 34 percent).

The transport, transformation, and fate of input by nonpoint sources are more complex because the nutrients must move from the basin land surface to the stream. The accounting procedure used in this mass balance exercise makes no provision for the reduction of nutrient load by transformation or storage before delivery to the stream.

Phosphorus

Total basin phosphorus inputs ranged from 9.8 to 72 percent from atmospheric deposition (26 percent

mean), 7.1 to 51 percent from crop fertilizer (28 percent mean), 20 to 64 percent from animal waste (41 percent mean), and 0 to 22 percent from point sources (5.3 percent mean, Table 10; Figure 7). Animal waste was the largest phosphorus input in 12 of the 18 subbasins (Table 10). The Etowah River (Site 1; 64 percent of total inputs), the Alabama River (Site 9; 52 percent), the Black Warrior River (Site 17; 52 percent), the Coosa River (Site 4; 50 percent), the Tombigbee River (Site 18; 49 percent), and the Little Cahaba River (Site 7; 48 percent) were the subbasins with the highest phosphorus inputs from animal waste.

Dominance of animal waste inputs of phosphorus also was reported for the Albemarle-Pamlico drainage (Harned *et al.*, 1995). Reported input rates for the Upper Potomac (1.7 tons/mi²/yr) (Jaworski *et al.*, 1992) and the Albemarle-Pamlico Basin (0.82 tons/mi²/yr) (Stanley, 1989) were higher than those estimated for the Mobile River Basin (Table 3;

mean = 0.35 tons/mi²/yr) because of greater animal inventories in those areas.

Fertilizer inputs of phosphorus were the principal sources in three of the 18 subbasins (Table 10) – Tibbee Creek (Site 11; 51 percent), the Tombigbee River (Site 10; 44 percent), and the North River (Site 16; 38 percent). Atmospheric inputs of phosphorus were the principal sources in three of the 18 subbasins – Sipsey Fork (Site 15; 72 percent), the Etowah River at Allatoona Dam (Site 2; 39 percent), and the Etowah River at Rome (Site 3; 28 percent).

Point sources were an important input source of phosphorus in several subbasins (Table 10). The Etowah River (Site 3; 22 percent of total inputs), Cahaba River at Centreville (Site 8; 17 percent), Coosa River (Site 4; 11 percent), and the Cahaba River near Mountain Brook (Site 6; 10 percent) all had large point source phosphorus inputs (Table 10). The Etowah and Coosa Rivers are upstream from the nutrient sensitive Weiss Lake (Figure 1). The high phosphorus inputs for the Cahaba River Subbasin are

TABLE 10. Estimated Phosphorus Mass Balance as a Percentage of Total Inputs to the Mobile River Basin (–, no data).

Map No. (Figure 1)	Station Name	Point Source Input (percent)	Mean Fertilizer Input, Atmospheric Input (percent)			Animal Waste Input, 1997 (percent)	Crop Removal Output, 1990 to 1998 (percent)	Mean Instream Yield (percent)	Crop Storage (percent)
			1990 to 1998 (percent)	1997 (percent)	1990 to 1998 (percent)				
1	Etowah River at Canton, Georgia	0.31	28	7.1	64	1.3	36	62	
2	Etowah River at Allatoona Dam above Cartersville, Georgia	4.6	39	23	34	.34	27	72	
3	Etowah River at Rome, Georgia	22	28	26	24	5.1	30	64	
4	Coosa River near Rome, Georgia	11	22	17	50	7.7	34	58	
5	Alabama River near Montgomery, Alabama	4.8	25	27	43	3.8	11	85	
6	Cahaba River near Mountain Brook, Alabama	10	34	20	36	.0092	33	66	
7	Little Cahaba River near Jefferson Park, Alabama	1.7	19	31	48	.033	–	–	
8	Cahaba River at Centreville, Alabama	17	26	22	35	.54	22	77	
9	Alabama River at Claiborne, Alabama	5.8	21	21	52	5.0	15	80	
10	Tombigbee River near Fulton, Mississippi	.73	19	44	36	23	18	58	
11	Tibbee Creek near Tibbee, Mississippi	.45	9.8	51	39	11	13	76	
12	Luxapallila Creek near Columbus, Mississippi	1.9	25	36	37	9.9	9.6	80	
13	Noxubee River near Geiger, Alabama	2.7	19	36	42	20	30	50	
14	Tombigbee River at Gainesville, Alabama	1.8	17	37	45	17	–	–	
15	Sipsey Fork near Grayson, Alabama	0	72	8.7	20	1.1	14	85	
16	North River near Samantha, Alabama	3.2	30	38	29	5.9	14	80	
17	Black Warrior River below Seldon Lock and Dam near Eutaw, Alabama	4.8	19	24	52	2.9	13	84	
18	Tombigbee River below Coffeeville Lock and Dam near Coffeeville, Alabama	2.9	20	28	49	10	21	68	

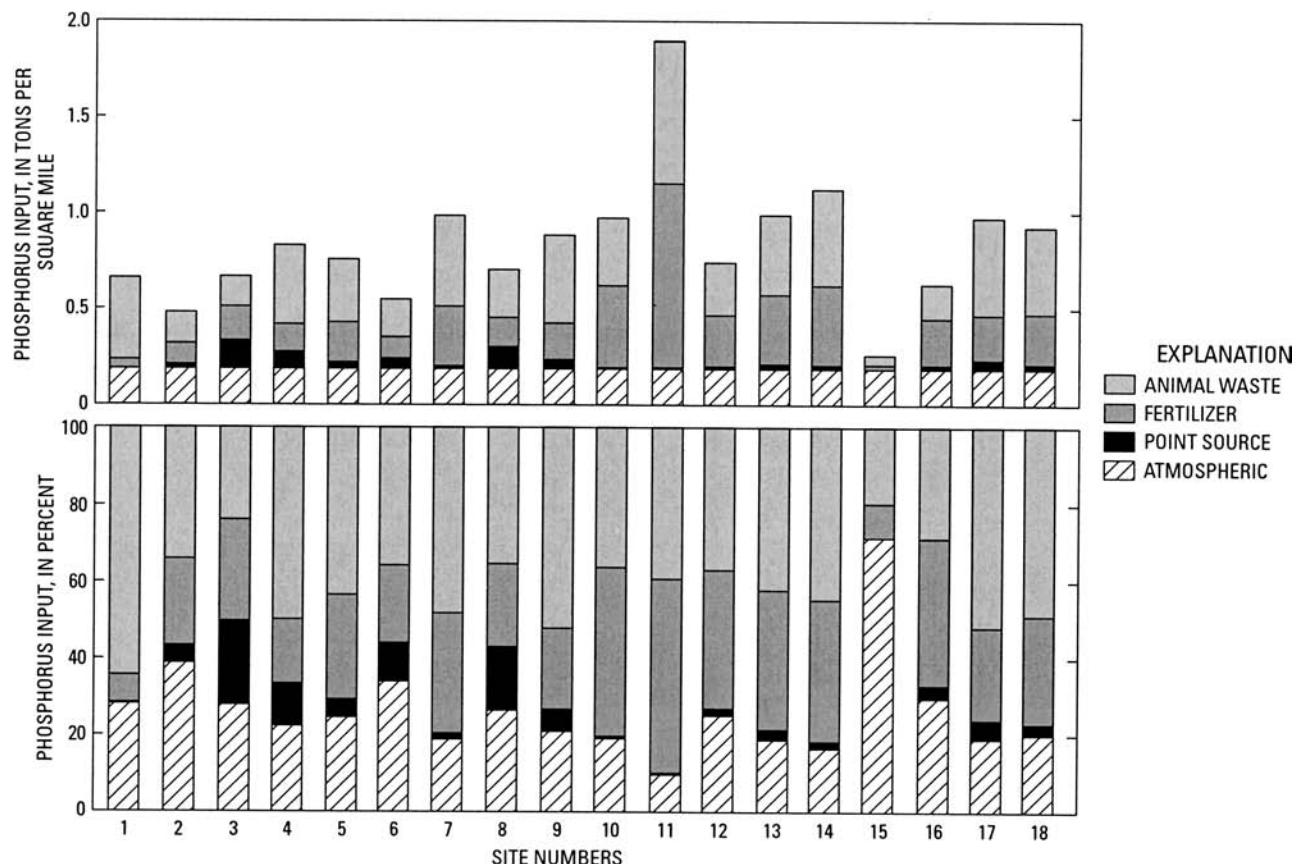


Figure 7. Phosphorus Inputs at Sites in the Mobile River Basin.

a result of urban development around Birmingham, Alabama. Thirty-one to 80 percent of the instream phosphorus yield may be accounted for by point source inputs alone for the Cahaba River (Site 8; 80 percent), Etowah River at Rome (Site 3; 75 percent), Alabama River near Montgomery (Site 5; 43 percent), Alabama River at Claiborne (Site 9; 39 percent), Black Warrior River (Site 17; 39 percent), Coosa River (Site 4; 31 percent), and the Cahaba River near Mountain Fork (Site 6; 31 percent). Point source input rates of phosphorus estimated for the Mobile River Basin are similar to those reported for the Albemarle-Pamlico Basin (Stanley, 1989; Harned *et al.*, 1995) and the Upper Potomac River Basin (Jaworski *et al.*, 1992).

Basin Nutrient Storage and Processing

The largest values in the mass balance for both nitrogen and phosphorus were for storage in the Mobile River Basin. From 33 to 85 percent (mean 69 percent) of nitrogen inputs were retained in the 18 subbasins (Table 9). Retention of phosphorus inputs

ranged from 50 to 85 percent (mean 72 percent; Table 10). Input/output analysis highlights the points in the nutrient cycle where nutrient amounts can be qualified easily, records are available for input sources, or stream sampling allows quantification of outputs from the basin. However, a great deal of information is missing in any such analysis. Nutrient storage in a basin, in the form of long term storage in plant tissue as organic nitrogen or phosphorus; movement of nitrate into the deep ground water flow system; and adsorption of phosphorus onto soil and sediment particles may help to explain the huge difference between what is accounted for as nutrient input and what is measured as nutrient output. In addition, nutrient processing, primarily by nitrogen reducing bacteria in anoxic environments such as soil and wetlands, converts nitrogen compounds to nitrogen gas, which is cycled back into the atmosphere. It is important to note that studies aimed at quantifying the storage and retention components of the mass balance suggest that basins do have an impressive capacity to intercept much of the additional loads of nutrients from agriculture and urban development. For example, Jaworski *et al.* (1992) concluded that 66 percent

of the total nutrient inputs were either lost to the atmosphere or stored in the basin soil, ground water, or biomass. A reduction of 66 percent of inputs of non-point source nutrients from the mass balance calculation again highlights the importance of point-source inputs. Clearly, how nutrients are stored and processed in the basin and how storage and processing can be enhanced through environmental management actions are important questions.

Correlation Analysis

Correlation analysis allows a test to check if instream nutrient levels are indeed significantly associated with basin activities. Basin land use was used as the indicator of the type of basin activity. Correlation of basin nutrient yields and concentrations (dependent variables) with basin inputs and land use (independent variables) was tested by using the non-parametric Spearman rank test. The significant correlations are given in Table 11. Several of the sites are nested within other subbasins; serial correlation of these sites was not accounted for in this analysis.

The correlation analysis indicated that high nitrogen concentrations in the streams are associated with high percentages of urban areas in the subbasins. The mean nitrogen concentration for each subbasin had a significantly positive (probability < 0.05) correlation with basin percentages of low-density residential area, high density residential area, grass (including residential), total urban area, and commercial and industrial area.

High phosphorus concentrations were correlated with agriculture. High mean phosphorus concentrations for each subbasin were significantly correlated

with greater nitrogen fixation, crop removal of both nitrogen and phosphorus, and land area in pasture. Increasing phosphorus yields were significantly correlated with increasing subbasin area in pasture, and subbasin phosphorus concentrations increased with increasing pasture area, nitrogen fixation, and crop removal of both nitrogen and phosphorus. Counter intuitively, phosphorus concentrations had no significant correlation to point source inputs although the source analysis showed that point sources are an important source of phosphorus in the more urban basins. This analysis suggests that agricultural activities play an important role in the amount of phosphorus available instream, possibly due to phosphorus adsorbed to sediment transported to the streams with agricultural activity.

TRENDS

Long term (decadal) trends in water quality reflect large-scale anthropogenic influences, including long-term changes in land use and changes in resource management. Short term (annual) trends reflect more transient variables, including economic changes in agriculture and alteration of industrial or municipal wastewater treatment processes. USGS surface water sampling sites in the Mobile River Basin were reviewed for available nutrient data for the period 1970 to 1997. Sites having sufficient nutrient data were evaluated for long term trends in nutrient concentrations. The short term trend variation for these sites was correlated with annual variation in agricultural nutrient input sources to better define the relation between agricultural practices and streamwater quality.

TABLE 11. Results of Spearman Rank Correlation of Nutrient Yields and Concentrations With Basin Inputs and Land Use for the Mobile River Basin (N = number of samples).

Dependent Variable	Independent Variable	Spearman Rank Correlation Coefficient	Probability	N
Nitrogen Concentration	Low Density Residential	.63	.015	14
Nitrogen Concentration	High Density Residential	.62	.017	14
Nitrogen Concentration	Grass	.60	.022	14
Nitrogen Concentration	Urban	.57	.032	14
Nitrogen Concentration	Commercial and Industrial	.56	.038	14
Phosphorus Concentration	Nitrogen Fixation	.51	.032	16
Phosphorus Concentration	Crop removal of Nitrogen (1990 to 1998)	.53	.040	16
Phosphorus Concentration	Crop removal of Phosphorus (1990 to 1998)	.51	.044	16
Phosphorus Concentration	Pasture	.50	.047	16
Phosphorus Yield	Pasture	.53	.033	15

USGS sites having periods of continuous streamflow and nutrient data for the period 1970 to 1997 were examined for long term trends with the seasonal Kendall trend test. Trends were examined for total nitrogen at 15 sites and for total phosphorus at 14 sites. The seasonal Kendall trend test adjusts for seasonal variability by using nutrient concentrations adjusted for the effects of streamflow with residuals from LOWESS (LOcally Weighted Sum of Squares) smoothed curves (Hirsch *et al.*, 1982; Helsel, 1993). Trends also were determined for sites without continuous data by using multivariate regression analysis.

The general pattern observed in total nitrogen concentrations for the 1975 to 1996 period is an increase in concentration until about 1987 followed by a decrease. This pattern occurred at six of the sites (Figure 8) and was apparently driven by a change in total organic plus ammonia nitrogen (Figure 9), which shows a similar increase and decline over the same period. No trend was apparent in dissolved nitrite plus nitrate concentrations (Figure 10). The decrease in organic nitrogen in the streams may be a result of more effective municipal wastewater treatment during the 1980s.

The Alabama River (Site 9) and Tombigbee River (Site 18) were used to represent the most downstream locations in the Mobile River Basin. A significant trend of decreasing concentrations of total nitrogen was identified at both of these sites for the period 1988 to 1996. The trend suggests an overall reduction in nitrogen contributions to Mobile Bay from the Mobile River from the mid-1980s to the mid-1990s. Total nitrogen concentrations also have decreased (1980 to 1995) in the Black Warrior River (site 17), one of the major tributaries to the Tombigbee River. However, increasing trends (1988 to 1996) were detected in the Alabama River (Site 5) and the Cahaba River (Site 8, both heavily influenced by upstream urban development).

The general pattern observed in total phosphorus concentrations for the 1972 to 1996 period is a decrease in concentration, especially from 1977 to 1985. This pattern is evident at four of the sites (Figure 11). The removal of phosphate from household detergents is likely the reason for much of this decline.

Total phosphorus concentrations increased from 1988 to 1996 at three sites on the Etowah River in Georgia, probably as a result of urban development. The amount of urban and residential development in the Etowah River Subbasin at Rome (Site 3) is approximately 50 percent greater, in general, than in the Alabama River Subbasin. Declines in phosphorus concentration were detected at the Tombigbee River (Site 14) and the Little Cahaba River (Site 7) from 1988 to 1996.

A review of nitrogen and phosphorus trends for the Alabama and Tombigbee Rivers (McPherson *et al.*, 2003) includes data from 1978 to 2001. This analysis, which also used the seasonal Kendall trend test and LOWESS, shows a continued statistically significant general decrease in nitrate in the Alabama River from 1997 to 2001. Decreases in row crop agricultural activities and improved wastewater treatment were suggested as possible causes for the nitrate decline.

Association of Annual Variations in Water Quality and Agricultural Practices

To define the degree of association between agricultural practices and stream nutrient concentrations, annual variations in water quality data from the 18 subbasins in the Mobile River Basin were correlated with annual variations in crop amounts, fertilizer use, and farm animal counts. For this exercise, short term trends were used as a rough means of providing a model of the relation between agricultural practices and streamwater quality.

Annual measures of crop harvests, fertilizer sales, and farm animal populations were compiled to represent agricultural activities; however, these variables are highly intercorrelated. By using principal components analysis, several intercorrelated variables can be combined into a smaller number of synthetic variables. Analysis of annual county reports of crop acreages (1972 to 1998) for barley, corn, cotton, oats, peanuts, potatoes, sorghum, sweet potatoes, tobacco, and wheat yielded three principal component synthetic variables (SOY, CORN, and WHEAT-SORGHUM) that together accounted for 98 percent of the annual variance in crop harvest. The acreages of soybeans harvested is the dominant variable in the SOY principal component (loading = 0.98), acreages of corn harvested is the dominant variable in CORN (0.99), and acreages of wheat (0.71) and sorghum (0.68) harvested are the dominant variables in WHEAT-SORGHUM. A separate principal components analysis of data from annual county reports (1990 to 1998) of fertilizer sales for total amounts of nitrogen, phosphorus, and potassium, and estimates of total nutrient input amounts from fertilizer based on census of agriculture data yielded a single principal component (FERT) that accounted for 82 percent of the annual variance in fertilizer sales and estimated fertilizer use. County level farm animal counts of cattle, hogs, chickens, turkeys, sheep, and horses for 1982, 1987, 1992, and 1997 yielded two principal components (CHICKEN and CATTLE) that accounted for 99 percent of the annual variance in animal populations. The number of chickens is the dominant variable in the CHICKEN principal component (loading = 0.98),

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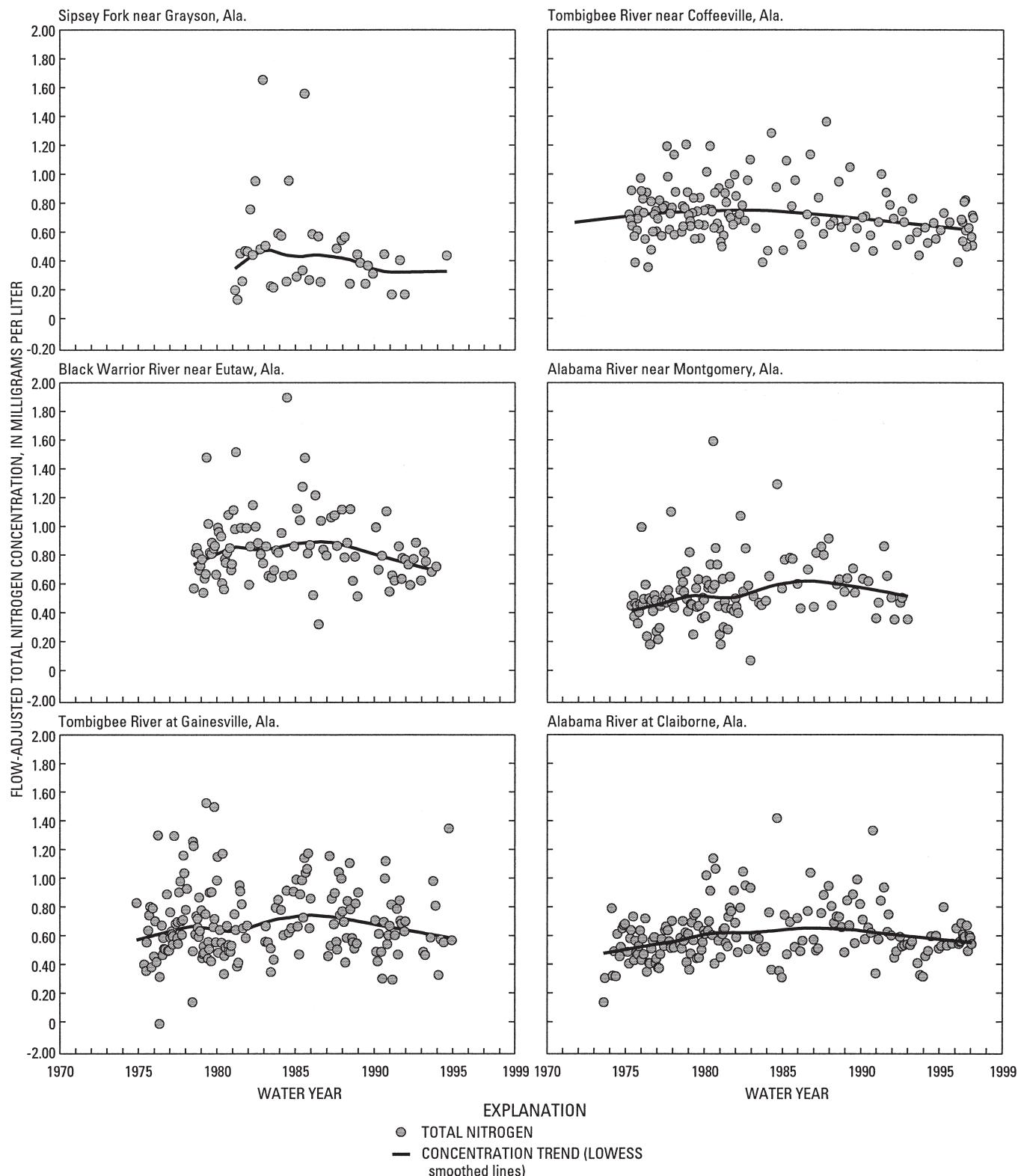


Figure 8. Trends in Flow Adjusted Total Nitrogen Concentrations at Selected Sites in the Mobile River Basin.
 (Water year is the period from October to September and is identified by the year in which it ends;
 e.g., October 1990 to September 1991 is the 1991 water year.)

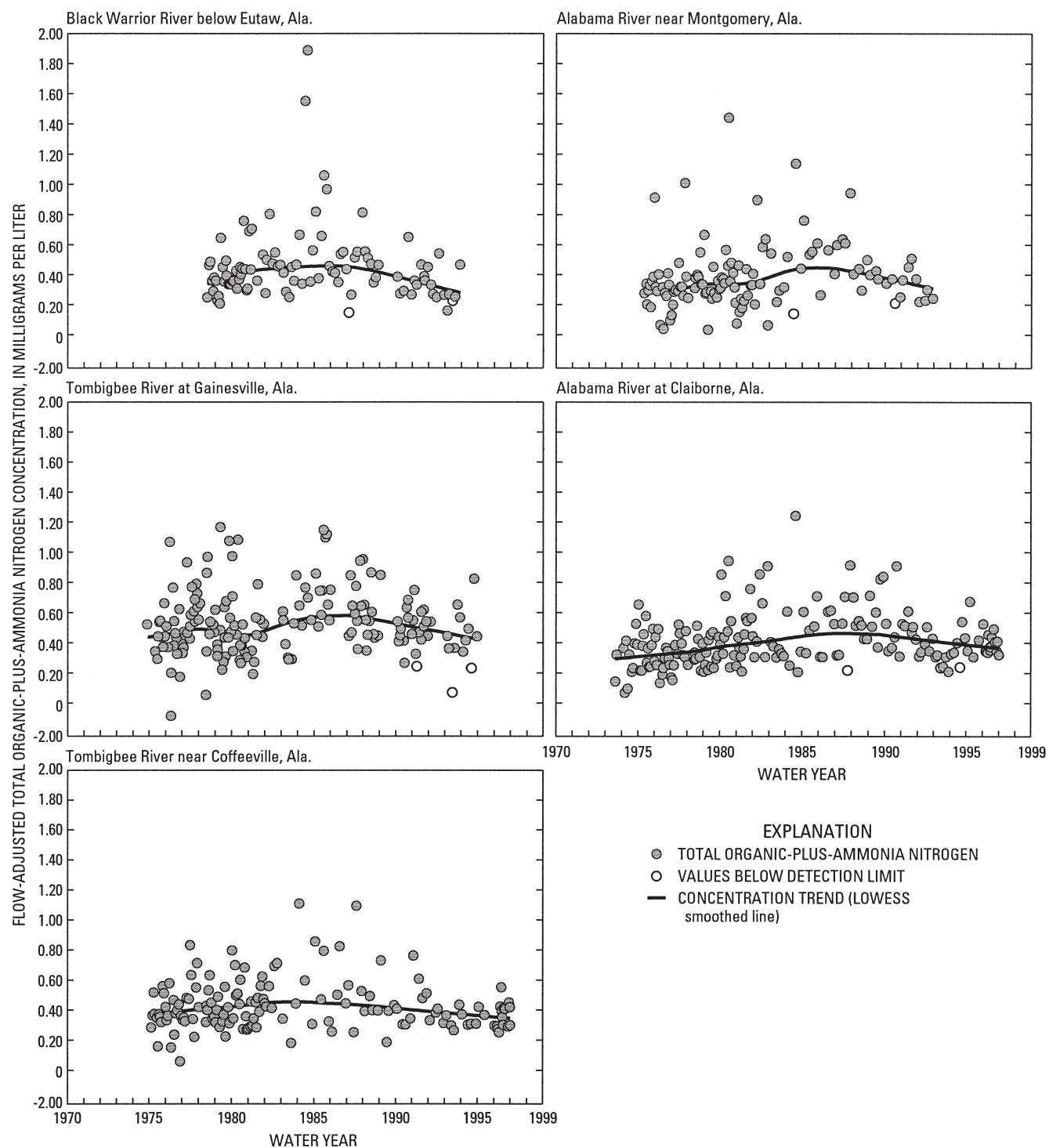


Figure 9. Trends in Flow Adjusted Total Organic Plus Ammonia Nitrogen Concentrations at Selected Sites in the Mobile River Basin. (Water year is the period from October to September and is identified by the year in which it ends; e.g., October 1990 to September 1991 is the 1991 water year.)

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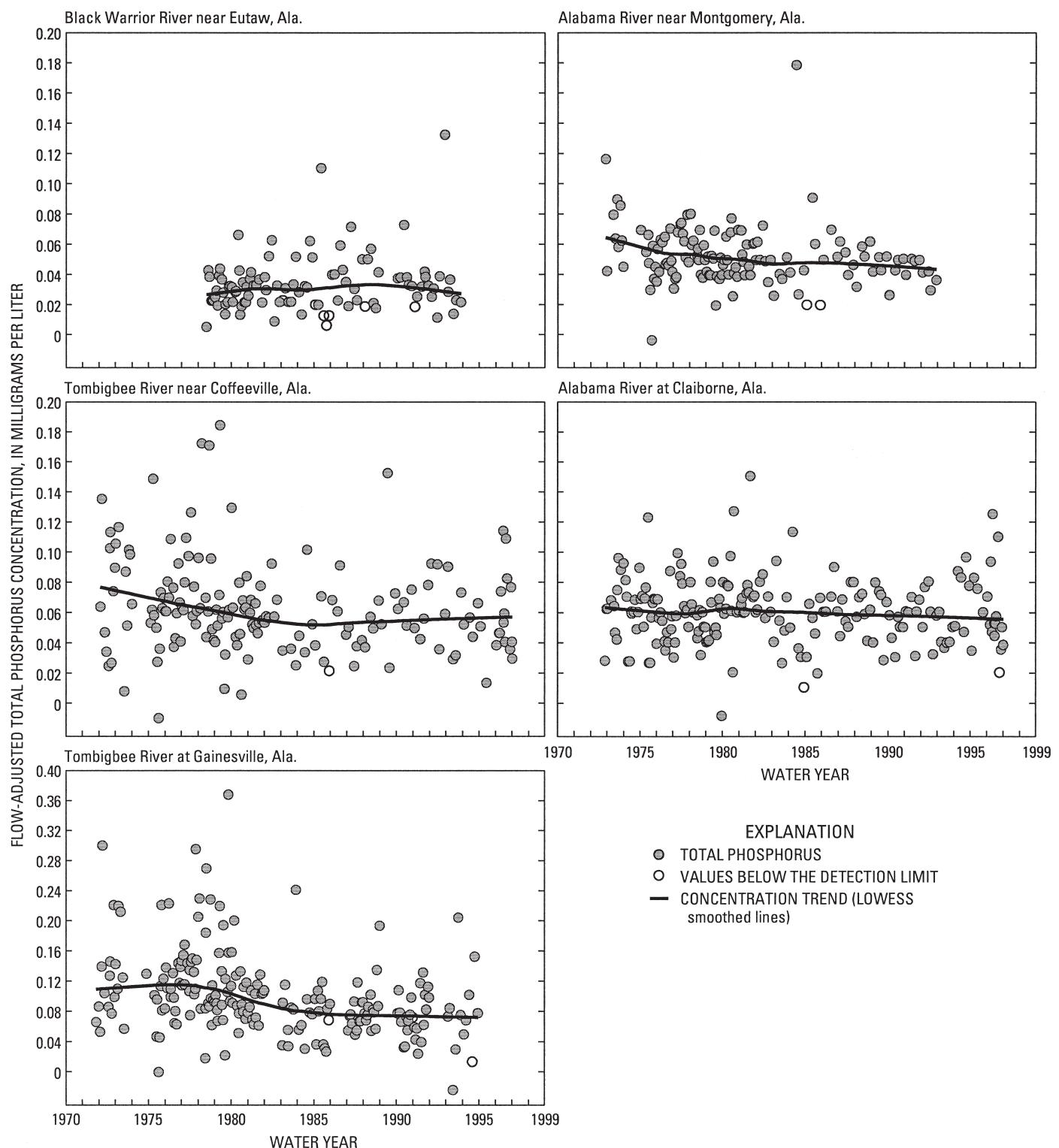


Figure 10. Trends in Flow Adjusted Dissolved Nitrite Plus Nitrate Concentrations at Selected Sites in the Mobile River Basin. (Water year is the period from October to September and is identified by the year in which it ends; e.g., October 1990 to September 1991 is the 1991 water year.)

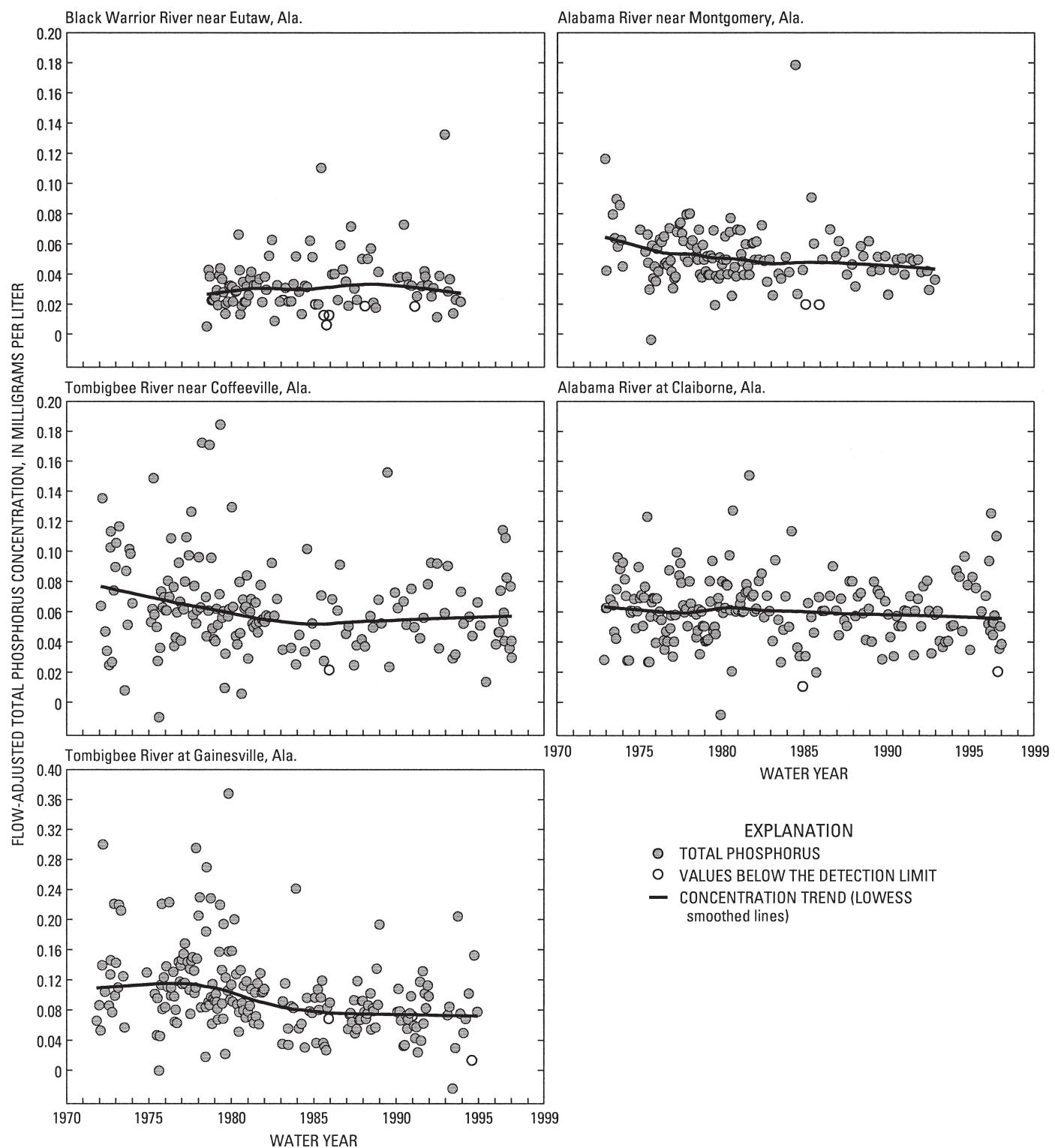


Figure 11. Trends in Flow Adjusted Total Phosphorus Concentrations at Selected Sites in the Mobile River Basin.
(Water year is the period from October to September and is identified by the year in which it ends; e.g., October 1990 to September 1991 is the 1991 water year.)

and the number of cattle (0.99) is the dominant variable in CATTLE.

Multiple regression analysis was used to test the association of the agricultural principal component variables (SOY, CORN, WHEAT-SORGUM, FERT, CHICKEN, and CATTLE) with streamwater quality. The mean, median, and maximum nitrate and total phosphorus concentrations were calculated for each year of water quality data for each subbasin and represent the dependent variables. Mean, median, and maximum streamflows calculated from streamflows at the time of sampling were included as variables in each regression to control water quality variations related to discharge, and a time variable was included to account for trends over time that were unrelated to agricultural or streamflow variables. The statistically significant ($\alpha = 0.05$) regression models for each independent measure of water quality (mean, median, and maximum nitrate and total phosphorus concentration) with the largest r^2 value, and one to three agricultural dependent variables were used to identify the agricultural variables most likely to affect streamwater quality. Multiple regression analysis was run once with the full suite of dependent variables, and a second time without the animal count variables because of the limited animal data.

The resultant regression models indicate a distinct association between water quality in the streams of the Mobile River Basin and agricultural activities (Table 12). The best-fit models that emerged when all dependent variables were tested are dominated by the animal count variables. The best models of nitrate for

mean, median, and maximum annual concentration included both the CHICKEN and CATTLE variables, clearly indicating an association of animal population and nitrogen concentration in the streams ($\alpha < 0.05$; $r^2 > 0.74$). Mean and maximum total phosphorus concentrations were associated positively with FERT amounts and negatively with CATTLE ($r^2 > 0.55$). When the animal variables were removed from the analysis, the best-fit model for mean and maximum nitrate showed time, maximum discharge, and FERT to be the most significant variables, and the model for median nitrate showed time, (-) CORN, and FERT to be the most significant variables ($r^2 > 0.34$). The counterintuitive inverse relation of the CORN variable with median nitrate may be a result of intercorrelation of the CORN variable with the FERT variable. The maximum total phosphorus concentration model included a negative term for maximum discharge and a positive FERT term ($r^2 = 0.24$).

CONCLUSION

A nutrient mass balance of the Mobile River Basin and a review of source and instream nutrient trends provide a framework for understanding nutrient accounting in the Mobile River Basin. An accounting of the nutrient sources highlights the importance of nitrogen inputs from atmospheric deposition, animal waste, fertilizer, and crop nitrogen fixation. Animal waste and point sources were important sources of

TABLE 12. Significant Variables in Multiple Regression Models Relating Several Annual Measures of Instream Nutrient Concentrations With Year, Measures of Annual Discharge, and Principal Components Analysis of Agricultural Variables [Bold indicates the models without the CHICKEN AND CATTLE variables; + indicates a statistically significant ($\alpha = 0.05$) positive coefficient; - indicates a statistically significant ($\alpha = 0.05$) negative coefficient; NS, no significant models].

Independent Variable	Dependent Variable			Total Phosphorus Concentration		
	Mean	Median	Maximum	Mean	Median	Maximum
Year	+	+	+			
Mean discharge						
Median discharge						
Maximum discharge	-		-			-
SOY						
CORN		-				
WHEAT-SORGUM						
FERT	+	+	+	+		++
CHICKEN	+	+	+			
CATTLE	+	+	+	-		-
R ²	0.76/ 0.31	0.74/ 0.34	0.75/ 0.24	0.55	NS	0.78/ 0.24

phosphorus. A simple accounting of sources, however, makes no provision for transformation or storage of nutrients by physical, chemical, or microbial processes. Point sources, which are delivered directly to the stream, are likely to have a greater effect on instream nutrient loads than is suggested by the relative load percentages. Thirty-four percent of instream nitrogen yield at two sites and 31 to 80 percent of phosphorus yield at seven sites could be accounted for by point-source inputs alone.

Correlation analysis indicated that high nitrogen concentrations in streams are associated with high percentages of urban development in the stream basins. In addition, high phosphorus concentrations are associated with upstream agricultural development.

Trend analysis indicated a long term pattern of increasing nitrogen concentrations until 1987 followed by a decrease, probably because of improvements in wastewater treatment. Phosphorus concentrations decreased from 1977 to 1985, probably as a result of the removal of phosphate from household detergents. An increase in total phosphorus (1988 to 1996) observed at several sites in Georgia most likely reflects a corresponding increase in urbanization.

Association of short term annual variations in streamwater quality and annual variations in agricultural nutrient sources was examined by using multiple regression analysis. The results provide further evidence of the close relation between agriculture and streamwater quality. Annual variations in animal populations and fertilizer amounts were associated with annual variations in instream nitrogen and phosphorus concentrations.

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Gerard McMahon contributed the basic methodology used in the source analysis. The authors also thank Lynn Sisk of the Alabama Department of Environmental Management for providing point source data. Editorial reviews were provided by Kay Hedrick and Rebecca Deckard.

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